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THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDATE-MAGNESIA METHOD.

BY B. W. KILGORE.

Received September 15, 1894.

FOR the investigation of the official molybdate method as used by the American Association of Official Agricultural Chemists for 1894, three samples were sent to various agricultural and commercial chemists with instructions for analysis.

No. 1 was a mixture of cottonseed-meal and castor pomace, containing about two and one-half per cent. P_2O_5.

No. 2 was an acid phosphate with about seventeen per cent. P_2O_5.

No. 3 was a phosphate solution containing ten grams C. P. disodium hydrogen phosphate ($Na_2HPO_4 + 12H_2O$) to the liter, the theoretical percentage of P_2O_5 in this salt being 19.826.

The discussion, which will be made here, of this work will be confined to the results obtained on solution No. 3, as it was the only sample whose content of P_2O_5 was definitely known. Twenty-eight chemists reported thirty-four determinations on No. 3, the highest of which was 20.67 per cent., and the lowest 19.74 per cent., the latter being 0.086 of one per cent. below the theory, and the former 0.844 per cent. above. The average of all results was 20.09 per cent., or 0.264 of one per cent. above the theory; the variation between highest and lowest results was 0.93 of one per cent.; the variation below the theory was 0.086 and above the theory 0.844 of one per cent. Eighteen per cent. of the determinations were within 0.05 of one per cent. of the theory, thirty-six per cent. within one-tenth, and forty-four per

cent. within two-tenths. In the work on this sample a few analysts have gotten results reasonably close to the theory, a great many have varied widely from it, and nearly all have gotten high results, which brings me to the point to which I desire to draw especial attention, and that is the tendency of the molybdate-magnesia method to give high results, even when the greatest care is exercised as is reasonable to suppose was the case in this test work. I might add here that nearly all the chemists taking part in this work had had some years experience with the method, and those who had not, worked under good supervision.

The tendency of the method then, it seems, is for high results, and it is in order to ask where the trouble lies.

The phosphate solution sent out was precipitated directly with magnesia mixture by four chemists, when they obtained (1) 19.92, (2) 19.93 and 19.94, (3) 19.91 and 19.85, and (4) 20.03 and 20.05 per cent. P_2O_5, against (1) 19.93 and 19.87, (2) 19.93 and 19.91, and (3) 19.93 and 20.06 by precipitating with molybdic solution first.

The results here by both methods of procedure, while slightly high, most of them, are practically the same whether precipitation was made direct with magnesia mixture, or previously with molybdic solution. This argues that the trouble is not in the molybdate precipitate or precipitation. The magnesium ammonium phosphate precipitate obtained from this sample in the usual way was, after washing, dissolved by one chemist in hydrochloric acid and reprecipitated with ammonia, when he obtained 19.80 and 19.81 per cent. P_2O_5, while another added one gram citric acid to the alkaline solution in which the "white precipitate" is formed and obtained 19.83 and 19.83 per cent. P_2O_5 against 20.06 and 19.93 by the regular method.

The results by the last two methods of procedure are, while few, close to the theory and indicate that in the regular molybdate-magnesia method that either some of the magnesium of the magnesia mixture is thrown down as hydroxide and contaminates the precipitate, or else the magnesium ammonium phosphate formed under the conditions of precipitation, contains more than a normal amount of magnesium, and that by dissolving the "white precipitate" in hydrochloric acid and reprecipitating,

and also by the presence of citric acid in the solution where the "white precipitate" is formed, the trouble is prevented.

H. Neubauer[1] has shown that magnesium ammonium phosphate formed in solutions containing an excess of both ammonia and magnesium salt, which is the condition of precipitation in the method under discussion, contains more than a normal amount of magnesium. The writer has had magnesium of the magnesia mixture to deposit as hydroxide and contaminate precipitates where very large excesses of the magnesia mixture were used in strongly alkaline solution and on long standing, though little or no error is thought to be introduced by this latter cause where the prescribed amount of magnesia mixture is used and too long standing not allowed. It is to the excess of magnesium in the magnesium ammonium phosphate, we consider, that the high results by the molybdate-magnesia method are due.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid" made by the writer to that association at its recent meeting.

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ON THE GUNNING METHOD FOR TOTAL NITROGEN IN FERTILIZERS.

BY W. E. GARRIGUES.

Received September 28, 1894.

COMPARED to the Scovell-Kjeldahl nitrogen method, that of Gunning, modified to include nitrates, does not seem to have met with the favor that its cleanliness and simplicity would warrant. It is believed that this is, in the main, due to the lower results consequent upon the use of the latter process; hence the following record of an investigation of its merits.

The work was commenced by running parallel analyses on fertilizers of unknown composition, containing sodium nitrate, by both of the methods named. In each case the manipulation, adopted by the Association of Official Agricultural Chemists,

[1] Abstract *J. Chem. Soc.*, of London, October *1893*, 489.

was rigidly adhered to. The appended figures, being the results obtained, speak for themselves:

Kjeldahl with zinc dust. Per cent. nitrogen.	Gunning with sodium thiosulphate. Per cent. nitrogen.
3.01	2.40 2.40
4.98	4.30 4.35 4.55
3.53	3.00 3.10 3.24
4.02	3.50 ....
4.67	4.05 4.21 4.24

A sample was then prepared from pure sodium nitrate and tankage. The latter was valued by the plain Kjeldahl and Gunning methods and by soda-lime combustion, with the following results:

Kjeldahl.	Gunning.	Soda-lime.
7.05	7.05	7.08

The calculated content of the mixture was 8.97 per cent. nitrogen, about one-half of which was in the inorganic form. On submitting this to analysis there were obtained:

Kjeldahl.	Gunning.
8.90	7.17
....	7.31
....	7.46

It was very evident that in the writer's hands the Gunning method, as adopted by the Association, did not convert all the nitrogen present into ammonia. After numerous and varied experiments, which, as is usual when viewed in the light of foregone events, now seem to have been largely unnecessary; successful results were finally obtained by using the same reagents, both kind and quantity, but varying the mode and order of their addition.

For convenience of reference the official directions from Bulletin 38, U. S. Dept. of Agriculture, are here given:

"In a digestion flask holding from 250 to 500 cc. place from 0.7 to 2.8 grains of the substance to be analyzed according to the amount of nitrogen present. Ten grams of potassium sulphate, five grams of sodium thiosulphate, and thirty to thirty-five cc. of the salicylic acid mixture, *i. e.*, thirty cc. of sulphuric acid to one gram of salicylic acid, are then added and the whole digested at a low temperature until frothing ceases."

The above unsatisfactory, or rather useless, results were

obtained in this manner. The chief fault is in the addition of potassium sulphate at such an early stage in the process; the large quantity of dry powder forming an effectual blanket over the sample, that for some time resists the permeation of the viscid acid solution.

The best procedure was found to be: Adding the salicylic acid mixture directly to the sample in the flask, which is then shaken until the liquid has thoroughly wetted the dry organic matter, allow to stand about fifteen minutes, and add the thiosulphate with constant shaking. This should be done in four or five portions, following with a fresh crystal only when the one previously added has completely dissolved. The potassium sulphate is then put in and the whole again well agitated. Digest as usual.

Handled in this manner the known mixture above referred to, gave:

8.85
8.87
8.90
8.92

Another sample of dry bone tankage and sodium nitrate was prepared and passed several times through a sixty mesh sieve. The tankage was valued as before, and showed:

Kjeldahl.	Gunning.	Soda-lime.
4.32	4.32	4.39
4.40	4.42	....

The calculated content of the mixture was 6.49, and the analyses returned:

Kjeldahl.	Gunning.
6.45	6.43
....	6.45
....	6.45
....	6.46

Neither method gave results sufficiently accurate for the valuation of sodium nitrate alone; a carefully prepared sample of that salt showing on analysis:

Kjeldahl.	Gunning.
16.05	15.80
16.35	16.00
....	16.15
....	16.22
....	16.38

Theory 16.49

It will be noticed that without a single exception the returns of analyses were below the amount actually present. No means of avoiding this loss were found. It would, therefore, seem justifiable to report the highest figure in closely agreeing duplicates instead of the customary average.

Several blanks run through to determine the freedom from nitrogen of the reagents employed, gave from nil to 0.05 per cent. No corrections were made for this.

During the distillation in the Gunning process the solution frequently foams badly; so much so that unless the flame is turned very low, the froth rises into the connecting bulb. The addition of paraffin wax does not always overcome this difficulty, and to avoid it, the use of an ordinary thirty-two-ounce wash-bottle, in place of the 500 to 600 cc. distillation flask is recommended.

There is little doubt that the seat of responsibility for many minor discrepancies is imperfect prepartion of the sample. Attendant upon the use of the official twenty-five mesh sieve, variations in the hands of the same manipulator frequently reach 0.15 per cent., even when exceptional care is exercised. It has, therefore, been found advisable in nitrated goods to quarter down the twenty-five mesh sample to about two ounces and pass that through a sixty mesh sieve; when this is done, the difference in duplicate analyses rarely exceeds 0.05 per cent., and decinormal acid and alkali often fail to show any.

Occasionally it becomes necessary to dry the sample before it can be thus finely powdered; in that case making the moisture determinations of Stillwell and Gladding (Bull. 38, p. 19, U. S. Dept. of Agr.) is the best procedure, *i. e.*, weigh out a portion of about ten grams from the original package when first opened, and determine the total moisture in a water-oven, dry the remainder of the sample to dustiness, and prepare it as above; then weigh out two grams of the fine sample simultaneously with the portion to be used for nitrogen, and ascertain the remaining moisture. A simple calculation brings the nitrogen figure back to the original condition of the goods.

Usually, however, nitrated fertilizers contain only a few per cent. of moisture, as indeed they should, lest the free acid of

the phosphate in the presence of water, act on the easily decomposable salt and liberate nitric acid. This theoretic action has been found a sad reality by manufacturers who incorporated nitrate salts with a wet "super," the loss of plant food being accompanied by a destruction of the fiber of the bagging containing the goods.

FALLACIES OF POST-MORTEM TESTS FOR MORPHINE.[1]

By David L. Davoll, Jr.

Received August 9, 1894.

IN the qualitative investigations upon morphine in a former series of experiments, the tissue was allowed to putrefy in the open air, a condition which is not present in the case of a buried body, for in the unopened cadaver, the bacterial products are very different in their deportment toward certain reagents, from those formed by aerobic germs and are the interferences which would be met with in chemico-legal work and which give some of the tests for morphine.

The writer, during the spring of 1893, in a series of determinations to ascertain the minimum of loss entailed in the recovery of a weighed amount of commercial morphine sulphate—the form generally employed in instances of poisoning—from a given amount of putrefied tissue, obtained the following results by the method given in detail below:

A. From sixty grams of stale bread, containing 0.2387 gram of morphine sulphate, 0.0844 gram of anhydrous alkaloid were recovered, the equivalent of 0.2245 gram of morphine sulphate; this shows a loss of 0.0142 gram or 5.94 per cent. By qualitative tests upon $\frac{1}{500}$ part of this recovered amount, very decided affirmative results were obtained.

B. From 100 grams of fresh liver, containing 0.3455 gram of morphine sulphate, 0.1163 gram of anhydrous alkaloid were recovered, the equivalent of 0.3093 gram of morphine sulphate, a loss of 0.0362 gram.

C. From putrid liver (after standing ten days in the open air and in a warm place) charged, when fresh, with 0.442 gram of morphine sulphate, 0.111 gram of anhydrous alkaloid were

[1] Read at the Brooklyn Meeting of the American Association for the Advancement of Science, August, 1894.

recovered, corresponding to 0.2952 gram of morphine sulphate, a loss of 0.1468 gram.

After much experience with quantitative methods now in vogue, both in opium assay, and toxicological work I have used the method of titration of the alkaloid by standard acid and alkali, isolating the alkaloid by shaking out with primary amyl alcohol.

A careful review of the qualitative tests for morphine was first gone over, working with normal and decinormal solutions of the anhydrous alkaloid, in the form of sulphate. The figures here given, refer to the anhydrous alkaloid evaporated to dryness upon one spot in a porcelain dish.

Fröhde's Reagent.—See discussion below.

Iodic Acid, with starch paste, is sensitive to 0.00001 gram.[1]

Nitric Acid, gives deep orange color with 0.00001 gram. This reagent also produces a red coloration with certain volatile oils and resinous substances.

Ferric Chloride, in neutral solution gives deep blue color, said by Wormley to be sensitive to $\frac{1}{10000}$. Results with putrefactive tissue are given below by the writer.[2]

Ferric Chloride with *Potassium Ferricyanide*, is sensitive to 0.000005 gram.[3]

Tattersall's Test, with sodium arsenate, followed by other reagents, is very satisfactory. (For details, see "New Color Reaction for Morphine, Codeine, and Atropine," *Pharm. J. Trans.*, [3], **12**, 459–60.)

Many other tests were worked upon, but being for the most part confirmatory and quite intricate in their manipulation, they

[1] Blyth, 1885; Separation of Morphine from Animal Tissue and Fluids; Poisons, their Effects and Detection, 1, 278. Selvin has pointed out that amyl alcohol extracts from putrefied matters, "ptomaines," agreeing with morphine in setting free iodine from iodic acid.

[2] T. G. Wormley, 1885; Morphine, Micro-Chemistry of Poisons, second edition, 485–6, says "that the blue color produced by $FeCl_3$ upon morphine is discharged by free acids, caustic alkalies, and heat. The blue color may not make its appearance if foreign substances be present and it is open to fallacy."

[3] O. Hesse, Morphine, *Pharm. J. Trans.*, **18**, 801, says, "In the ferric chloride and potassium ferricyanide test for morphine, the action is due to the formation of pseudomorphine and potassium ferrocyanide.

$$8C_{17}H_{19}NO_3HCl + 8K_3Fe(CN)_6 = 4C_{34}H_{36}N_2O_6.2HCl + 6K_4Fe(CN)_6 + 2H_4Fe(CN)_6.$$

Pseudo-morphine is actually deposited if the solution is not too dilute and this substance being somewhat soluble in water, is the cause of the blue coloration."

were not applied in this work for reasons which the decisive results render obvious. The negative results in testing for morphine have always been regarded as more conclusive than the positive.

The object of this work was to demonstrate, as far as possible, to just what extent cadaveric alkaloids might respond to the generally recognized tests for morphine; and to this end, the ordinary manner of burial of a corpse was followed, and after exhumation the several parts of the body were subjected to exactly the same treatment that would be followed were morphine suspected to be present as a result of poisoning.

A collie (dog) was taken, weighing thirty-four avoirdupois pounds; was shot between the eyes on March 3rd, at 1.30 P. M. and placed in a tight pine-box, when the cover was screwed on. This was buried under five feet of soil, consisting of clay mixed with gravel, on the forenoon of March 5th. When buried, the body had already begun to give off a strong odor. The body was taken up on the morning of April 26th, after forty-five days burial, the usual spring weather intervening, the box being dry inside. Eight hours after disinterment, all the parts—portion of brain, heart, lung, kidney, liver, spleen, bladder and urine, stomach and contents, piece of intestine with contents—were separately macerating in diluted alcohol.

The weights of the several parts in grams were as follows: Brain, 45; heart, 173; lung, 200; kidney, 70; liver, 345; spleen, 28; bladder and urine, 105; stomach and contents, 450; intestine with contents, 130.

The odor from the opened cadaver was overpowering, particularly from the cranial cavity. All organs were soft, but retaining their form. The brain was of a semi-fluid consistence, and when, later, the liquid extract was shaken out with immiscible solvents it emulsified exceedingly.

The method of extraction, given below, includes some few modifications over the older method, none of which, however, were introduced without previous proof of their applicability to the recovery of the alkaloid, morphine. For convenience of reference in the following comments, the manipulation was divided into arbitrary stages, designated by Roman numerals.

I. The finely divided material is placed in a flask of suitable capacity, from which extends upward a glass tube, three and one-half feet long by one-fourth inch internal diameter; the arrangement provides for the constant alcoholic and acidulous strength during extraction, by air condensation. Enough diluted alcohol (by volume) is added to well cover the material and the mass made slightly acid with acetic acid. The digestion is made upon a long iron plate, heated by means of Bunsen burners, so placed, at intervals, that the flame should strike *between* the flasks and not *directly beneath* them. The flasks are placed in a row upon the hot plate, and further protected from direct heat of the iron plate by interposing match-sticks between the flask-bottom and the hot plate, and are virtually heated by hot air and not by the plate, the wood being such a non-conductor of the heat. The digestion is continued for one hour, the temperature, 70° C., being read from a thermometer immersed in the viscera. Then cool, remove to a funnel and filter through paper by means of a filter-pump, or strain through carefully washed muslin, rinsing the flask with successive small portions of diluted alcohol and passing washings through the tissue, previously well drained. Remove the mass to the extraction apparatus and repeat the process of extraction and filtration as before. Three extractions are accounted sufficient.

II. The alcohol is removed by evaporation upon the water-bath, stirring to promote vaporization and prevent the formation of a crust.

III. The measure of the residual aqueous liquid is now ascertained, and being of a sirupy consistence, is placed in a flask of suitable capacity and three volumes of ninety-five per cent. alcohol added; the evaporating dish is rinsed with seventy-five per cent. alcohol and the washings added to the liquid under analysis. Sulfuric acid, approximately fifty per cent., is added to slight acidulation and all is set aside for eight to twelve hours, agitating occasionally. It is then filtered by means of a filter pump, and the precipitate washed with successive small portions of seventy-five per cent. alcohol.

IV. Remove the alcohol from the filtrate by evaporation upon the water-bath, and dilute with just sufficient water to obtain a

limpid consistence. The presence of much fatty matter may necessitate filtration; maintain the acid reaction.

V. The acidulous solution is now shaken with successive small portions of water-washed chloroform, until, upon evaporation, the chloroform solution leaves no appreciable residue; the miscibility of the so-called immiscible solvents causes a slight residue to remain upon evaporation, even after the chloroform has performed its work.

VI. Now shake out the acidulous solution with a cold amyl alcohol. These two solvents (V and VI) remove coloring and fatty matter. The chloroform and amyl alcohol washings should be shaken with slightly acidulated water and this latter added to the original liquid under analysis.

VII. The liquid is now made alkaline with ammonia water of sp. gr. 0.962 at 15° C. and shaken out with several successive small portions of chloroform and ether (three parts to one), this to remove cadaveric alkaloids as much as possible; this was suggested by the solubility of the cadaveric alkaloids in these media and the insolubility of the morphine in the same. This is repeated four times, the aqueous liquid being each time acidulated, the immiscible solvent added, shaken, and again rendered alkaline before the solvent has time to separate into a layer; this is done in order to obtain the alkaloids nascent.

VIII. (*a*) The same conditions of acidulating, adding hot solvent and making alkaline were observed here as in "Stage VII." The suspected (acid) is heated to 70° C., placed while hot in a separatory-funnel, and when alkaline, shaken out with successive small portions of hot amyl alcohol, until a small portion, upon evaporation, gives negative results with some delicate test, three to five shakings being generally enough.

(*b*) The amyl alcohol solutions are mixed, filtered, and then shaken with successive very small portions of water until no precipitate is afforded with barium chloride.

IX. It is then evaporated to dryness upon the water-bath and the residue taken up with slightly acidulated water, fiftieth normal sulphuric acid being the strength employed.

X. Filter this liquid, heat to 70° C., and shake with two successive portions of hot amyl alcohol in *acid* solution, mixing the

amyl alcohol washings and agitating with a little acidulated water, which is added to the liquid under analysis. This is done to further remove coloring matter. See remarks further on.

XI. Heat again to 70° C., add hot amyl alcohol, shake, render alkaline with ammonia water (0.962), again agitate and remove the amyl alcohol solution; repeat this extraction with hot amyl alcohol until all the alkaloid has been removed. Now repeat the shaking with water, as mentioned in "Stage VIII (*b*)" in order to remove ammonium sulphate.

XII. Four-fifths of the final purified amyl alcohol solution are evaporated to dryness upon the water-bath and titrated with fiftieth normal potassium hydroxide and sulphuric acid, using cochineal solution as indicator. The remaining one-fifth is tested qualitatively by all reliable methods.

The above is a detailed account of the method of extraction.

Guareschi and Mosso found commercial alcohol almost invariably to contain small quantities of an alkaloidal substance, having an odor similar to that of nicotine and pyridine. In amyl alcohol, Haitinger has found as much as one-half per cent. of pyridine. The ethyl alcohol and primary amyl alcohol used in this investigation were purified by distillation over tartaric acid, using five grams of acid to each 100 cc. of alcohol, the distillates coming over at 78° and 130° respectively. The basic substance which exists in some samples of ether is pyridine. The ether was water-washed, dried over calcium chloride and redistilled. Ether containing alcohol, as is well known, has a tendency to remove morphine from alkaline media. The chloroform was water-washed and redistilled. None of the above enumerated solvents, upon evaporation of fifty cc., yielded any appreciable residue, and upon applying reagents for morphine to the spot upon which the evaporation had been made, entirely negative results were obtained. "Stage VI" was omitted in extraction of all parts, excepting with liver, kidney, and intestines, since it was thought that, as morphine is removed from acid solution by amyl alcohol, it would be advisable to first purify the alkaloid by stages VII and VIII, thus leaving much coloring and extractive matter behind, and then to shake out the *hot* acid solution with successive portions of hot amyl alcohol, where a less amount

of the solvent need be employed and at the same time the very objectionable coloring matter would be more thoroughly removed. It was noticed in "Stage VI" that the *cold* amyl alcohol removed very little coloring matter, but that this same solvent, when *hot*, removed very much in "Stage VIII," which is avoided in "Stage XI." The reason why this method was not employed in the cases of the liver, kidney, and intestines, was that the idea did not suggest itself until after the final tests were applied to these. Before making this departure from the usual method the feasibility of it was first to be ascertained by actual experiment. One-half the final purified extractive matter from the liver was taken, in which negative tests for morphine had been obtained by Fröhde's reagent, Le Fort's test, and ferric chloride. Into this extract was introduced 0.0006 gram of morphine and all evaporated to dryness upon the water-bath; taken up with 100 cc. of fiftieth normal sulphuric acid, and this *hot* solution (acid) shaken out with twenty-five cc. of hot amyl alcohol. The solution was now shaken out with successive portions of twenty-five, twenty, and twenty cc. of *hot* amyl alcohol in alkaline media. The final measure was sixty cc. of purified amyl solution, each cubic centimeter of which *could not* contain more than 0.00001 gram of morphine. One cc. of this solution evaporated to dryness upon one spot gave very decided tests for morphine by Fröhde's reagent, which was the only test applied to the only perceptibly yellow residue. This test was as pronounced and strong as from 0.00001 gram of morphine evaporated from aqueous solution.

The stomach and heart yielded an extract of a very dark color, but by subsequent purification, particularly at "Stage IX," it was reduced to a very pale yellow, and, in fact, all extractive matter was freed from almost all color at this point, as the fiftieth normal sulphuric acid failed to appreciably effect the dark residue left at this stage. This residue needs some further mention; it was brownish to black in color, somewhat resinous and plastic in consistence; when not abundant it appeared as a brownish cryptocrystalline residue, taken up to a considerable extent by the fiftieth normal sulphuric acid. By computation it will be seen that 100 cc. of fiftieth normal sul-

phuric acid is capable of saturating 0.57 gram of anhydrous morphine, $C_{17}H_{19}NO_3$; or 0.606 gram of crystallized alkaloidal morphine, $C_{17}H_{19}NO_3,H_2O$, corresponding to 1.516 grams of morphine sulphate, $(C_{17}H_{19}NO_3)_2H_2SO_4.5H_2O$.

After treating with fiftieth normal sulphuric acid the solution is filtered through paper.

The final purified solution treated as above, is almost colorless at "Stage XII," and the residue left upon evaporation was, in the case of the brain, almost colorless: light yellow with all others, excepting the heart and stomach, which were yellow to light-brown.

The filtered liquid, after performing "Stage IX," was tested for alkaloids by bromine water, Wagner's solution, Mayer's reagent, sodium phosphomolybdate, and picric acid and all parts of the viscera gave strong precipitates with each reagent, excepting picric acid. The cautious addition of ammonia water to them also gave cloudiness.[1]

The reagents for the final identification tests were prepared for the most part after the directions given in "Reactions" by F. A. Flückiger, translated, revised, and enlarged by J. B. Nagelvoort.[2] Fröhde's reagent was made of the strength 0.010 gram of molybdic acid to each cubic centimeter of sulphuric acid, sp. gr. 1.84, and dissolved by digesting below 150° C.

The nitric acid test, ferric chloride with potassium ferricyanide, and the ferric chloride test were of the above recognized strength (Flückiger).

Le Fort's test was applied as follows: Iodic acid in solution is applied to the dry residue and all intimately mixed; chloroform, in successive small portions, is floated over this until it ceases to remove the pink color of iodine, the chloroform solution being removed by absorption with filter paper; one drop of ten per cent. ammonia water (or until alkaline) is now added and morphine will give a deep "mahogany color" not affected

[1] For a discussion of the production of precipitates with organic matter by such general alkaloidal reagents as Wagner's solution, Mayer's reagent, bromine water and picric acid. See T. G. Wormley, 1885; Morphine, Micro-Chemistry of Poisons, second edition, 492.

[2] Schönn, *Ztschr. anal. Chem.*, **8**, (*1869*), 379., in regard to preparing Fröhde's reagent says: "A moderate heat only should be applied, since the molybdic acid is reduced to a blue precipitate by heat alone at the temperature of incipient vaporization of H_2SO_4."

by chloroform, but changing back to yellow with hydrochloric acid. 0.00001 gram of pure morphine will respond to this test but the writer would not claim such extreme delicacy of reaction in presence of foreign matter; 0.00005 gram gives a good decided test, suitable for recognition in recovered matter.

After somewhat extended work upon morphine in the viscera, it seems to me that under the conditions mentioned, Fröhde's reagent, Le Fort's test, and ferric chloride are the least fallacious of all recognized tests applied.

Fröhde's reagent is especially satisfactory, appearing immediately as a deep purple color, fading to violet, then green, when applied to extractive matter *known* to contain morphine, and under these conditions sensitive to 0.00001 gram. In applying this test two samples, each containing extract from two cc. of the purified amyl alcohol solution were evaporated upon one spot in a porcelain dish upon the water-bath; to one of them was first added, and intimately mixed, 0.00001 gram of alkaloid morphine; the test was applied to both samples at the *same time* and in no instance was there obtained any indications whatsoever of morphine in the sample of extract *not* containing that alkaloid, a light green color only, appearing; but, on the other hand, the sample to which 0.00001 gram of morphine *had* been added, never failed to give a decided purple color *immediately*. These parallel tests were made for the purpose of verifying the conclusion, that, had morphine (or an alkaloidal base acting similarly toward Fröhde's reagent) been present in even so small an amount as 0.00001 gram a reliable test would have been obtained.

With ferric chloride, freshly dissolved and free from acid, the same parallel tests were made as with Fröhde's reagent, with the exception that 0.00005 gram of morphine was introduced in the comparative test, since this test is not as delicate as the molybdate in extractive matter. When applied to the extractive to which morphine had been added, bluish rings appeared, a positive test; but with the pure extract, from all parts of the viscera, no color appeared.

Le Fort's test was applied with a parallel test, containing 0.00005 gram of morphine and was very satisfactory as a reagent,

and as far as demonstrating the absence of morphine or any interfering bases was concerned, was conclusive. With the extractive to which morphine *had* been added, a final "mahogany color" had been obtained, but no change with the pure extract from the parts of the body.

Iodic acid gave indications of a reducing agency, since iodine could be detected with clear, fresh starch-paste in all instances.

The nitric acid tests were found to be of no value, ferric chloride, with freshly prepared solution of potassium ferricyanide, gave indications of a base having similar reducing action as morphine. Parallel tests were made, the one containing the extractive from two cc. of final amyl alcohol solution, was evaporated to dryness, taken up with four cc. of fiftieth normal sulphuric acid; the other treated in an exactly similar way, *but* to which had been added 0.00001 gram of morphine. To both these solutions were added eight cc. of a solution of potassium ferricyanide and one drop of solution of ferric chloride. With the portion known to contain morphine, a blue color appeared *at once;* with the simple extractive matter from the viscera, only a light green color appeared, not changing at all in three minutes; slightly darker in five minutes; after ten minutes one could easily distinguish the samples one from the other, but after two hours both had deposited a similar blue precipitate.

During the process of extraction of the different organs, it was noticed that from them, and particularly from the liver, brain, spleen, intestines, and kidney, a decided odor resembling that of trimethylamine was given off, continuing all the way through.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
June 2, 1894.

FERMENTATION OF GLUCOSE SYRUPS.

BY HORACE E. HORTON.

Received October 23, 1894.

I WOULD like to call attention to the interesting fact that glucose syrup of 41° Bé. is fermentable. The opinion is general that glucose of this gravity is non-fermentable and I am unable to find any published record of such fermentation.

During the summer of 1893 large quantities of the so-called "mixing glucose" sold in southern cities was found to be in a

state of active fermentation. It was thought that the samples were of light gravity, but moisture determinations showed 21.1 per cent., the normal quantity for 41° Bé. syrup. This fermentation was found to exist not alone in the 41° syrup but in samples of 42° Bé. containing 20.19 per cent. moisture.

Cultures of the various liquors in the refinery showed that the ferment was introduced into the goods at some point after the 39° Bé. vacuum pan.

To prevent the finished goods from fermenting the following experiments were made with well-known antiseptic materials.

1.46 pounds of 40° Bé. sodium bisulphite added to each barrel of fifty-two gallons. No effect.

One-half ounce boracic acid and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

1.46 pounds of 40° Bé. sodium bisulphite, one-half ounce boracic acid, and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

TOPEKA, KANSAS, October, 1894.

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.

BY LAURA A. LINTON.

Received September 21, 1894.

IN the year 1837, J. B. Boussingault published his celebrated memoir on the "Composition of Bitumens." In the researches upon which this memoir was based he had discovered that certain bitumens yielded to one class of solvents a portion of their content and to another class of solvents another portion of their constituent hydrocarbons. He called the first portion "Petrolene" and the second portion, "Asphaltene."[1]

In 1827[2] Le Bel and Muntz went over the same ground and in 1883 Le Bel again went over it, adding a few facts in relation to other bitumens than those previously examined but leaving the two substances, petrolene and asphaltene, practically where he found them.[3]

In 1837 the conclusions based on chemical research were far less exact than at the present time and Boussingault concluded that the substances, petrolene and asphaltene, were simple sub-

[1] *Annales de Chemie et de Physique*, **64**, 141.
[2] *Bull. Soc. Chim.*, **17**, 156. [3] Ibid, **50**, 359.

stances and also that they were identical from whatever sources they were derived. In this conclusion Le Bel in a measure appears to coincide.

It, however, requires no argument to prove, to any one at all familiar with the subject, that petrolene is nothing but a name that covers a great variety of substances, radically unlike, that exist in different forms of bitumen and are only related, in this instance, as being held in solution by a certain limited number of menstrua and which include the whole list of paraffines and iso-paraffines, the olefines, the benzenes and additive benzenes with many other less abundant and well-known substances.

Ethyl ether and so-called petroleum naphtha, which latter is an indefinite mixture of fluid paraffines and iso-paraffines of high specific gravity, are the solvents used; but no determination has been made as to the influence of proportion in the mixtures of the substances dissolved, or as to the relative solvent powers of the two menstrua upon the different constituents of these mixtures. In fact petrolene is nothing but a name which at present covers a vast expanse of the unknown.

It can be safely said that probability favors the assumption that asphaltene is a little more definite; but no certainty attaches to the identity of asphaltene from different sources or of asphaltene dissolved by different menstrua.

Therefore, in a general way, it may be said that asphaltene is that portion of the different forms of bitumen that is soluble in carbon disulphide, chloroform, benzene and a few other less well-known liquids and is not soluble in the menstrua that dissolve petrolene.

As the bitumens examined by the French chemists, above mentioned, have never assumed commercial importance, the questions relating to petrolene and asphaltene have remained matters of scientific interest only. However, since asphalt paving has become a business involving the expenditure of large sums of money these problems are beginning to assume a wide importance outside the laboratory of the chemist and to demand from technologists very serious consideration. Within recent years large numbers of so-called analyses have been reported, which represent various attempts to determine and set forth the rela-

tive value of many samples and kinds of asphaltum, that may or may not be suitable for the many uses to which asphaltum is applied, but more particularly with reference to street paving. Prominent among the chemists who have been more or less extensively engaged in these analyses of asphalts are Mr. Clifford Richardson, Dr. Henry Leffmann, Dr. Samuel P. Sadtler, and Dr. De Smedt.

A perusal of the numerous published reports of Mr. Richardson reveals the fact that in his tests the solvents used for the extraction of petrolene and asphaltene, were petroleum ether and carbon disulphide, while Drs. Leffmann and Sadtler, in their investigations and tests of asphalts, used alcohol—presumably ethyl-alcohol—carbon disulphide, and ether as shown by the report submitted to the Citizens' Municipal Association and the Trades League of Philadelphia.

Neither of these gentlemen describe any process or method employed in obtaining the results stated. It is hardly consistent with the nature of the reports that they should. Nor has Mr. Richardson, in an article published in the *Journal of Analytical and Applied Chemistry*, in the numbers for December, 1892, and January, 1893, given any detailed description of the process he employed in order to obtain the numerous results of analysis that he there uses.

But little satisfaction can be derived from consulting Allen's encyclopedic work so exhaustive upon every subject relating to technical organic analysis.[1]

We find therein the following statements and notes concerning the solvents and methods used in the analysis of asphalts: "For the determination of the *total bituminous matters* in asphalt rock and mixtures containing it, C. T. Kingzett extracts the air-dried sample with freshly distilled Russian oil of turpentine, evaporates (*Analyst* **8**, 4) the resultant solution and weighs the residue. The matter insoluble in turpentine is washed with ether, the *calcium* and *magnesium* carbonates dissolved in hydrochloric acid and the washed insoluble *siliceous matter* weighed."

"H. P. Cooper prefers carbon disulphide for dissolving out the bituminous matters from asphaltic mixtures."

[1] Commercial Organic Analysis, by Alfred H. Allen, London, *1886*, **2**, 375, 376, 377.

Allen adds in a note, "The carbon disulphide employed for dissolving the bituminous matter must not contain free sulphur. It may be replaced by chloroform or benzene (coal tar naphtha). If the residue left after extraction be dark colored, foreign organic matters of valueless nature are present. Their proportion may be determined by igniting the weighed residue left after dissolving out the asphaltum, recarbonating it with ammonium carbonate, again gently heating it and reweighing. The loss of weight is the amount of *non-bituminous* organic matter present. In the case of samples leaving a white residue after exhaustion with carbon disulphide, the bituminous matter may be simply and accurately ascertained from the loss on ignition, taking care to recarbonate the lime before weighing."

In another note, page 377, he says: "Five grams of the finely divided sample were digested for one hour with fifty cc. of petroleum spirit (sp. gr. 0.7) and the mixture frequently agitated. The liquid is then boiled for a short time, decanted and the residue boiled with another quantity of twenty-five cc. of petroleum spirit. This treatment is repeated eight or ten times until the exhaustion is complete.

"E. Davies (*Pharm. Jour.*, [3], **14**, 394), reports that none of the organic matter in Val de Travers asphalt is insoluble in petroleum spirit."

Now, when we take into consideration the fact that turpentine, carbon disulphide, ether, chloroform, and benzene have been used indiscriminately by chemists in the extraction of asphaltene, the question very naturally arises are the results that have been and that are being obtained by these different methods of analysis strictly comparable—that is, are they convertible terms? Will the same asphalt treated with different solvents show in each case the same percentage composition? If not, then it is evident that asphalt taken from different localities and subjected to dissimilar methods of analysis cannot yield results of any value so far as purposes of comparison are concerned. Then again, if turpentine, carbon disulphide, and chloroform give a different proportion of asphaltene in the same asphalt it is just as evident that asphaltene, instead of being a definite

chemical substance, is a mixture, which mixture would doubtless vary in different asphalts.

It was for the purpose of determining whether petroleum ether (paraffines), California naphtha, and ethyl ether are interchangeable solvents of petrolene and whether turpentine, carbon disulphide and chloroform are interchangeable solvents of asphaltene that the research, the results of which are here given, was undertaken. That a series of such tests, faithfully carried out, should lead to the establishment of a method of analysis applicable to all asphalts and, at the same time, reveal something regarding the real nature of petrolene and asphaltene was inevitable.

The specimens analyzed were furnished me by Prof. S. F. Peckham, Chemist of the Union Oil Company of California, and were as follows:

1. *Crude Trinidad Asphaltum.*—From the Warren-Scharf Asphalt Company, of New York City. This specimen contained little or no water, as, for several months, it had been broken in small pieces, and so had lost the water which this asphaltum generally contains.

2. *Cuban Asphalt.*—A commercial sample obtained in New York City.

3. *Kuban Residuum.*—An artificial asphalt obtained from the distillation of Kuban petroleum from the western extremity of the Caucasus Mountains, Russia.

4. *Egyptian Asphalt.*—An Assyrian asphalt taken from the Dead Sea and imported into Egypt. This specimen was obtained in New York City.

5. *Asphaltic Rock.*—From Val de Travers, Switzerland. This asphalt was a sample of natural rock obtained at the office of Wm. H. Delano, representative of the French Company in New York City.

6. *Seyssel Asphaltic Rock.*—From the well-known locality in eastern France, obtained from the same source as No. 5.

7. *Turrellite.*—From a deposit lately discovered in Uvalde County, Texas, consisting of a mass of sea-shells cemented together by bitumen into a solid rock mass. It occurs in a rock formation said to be of Jurassic age, in which formation the Val de Travers rock also occurs. This specimen was obtained from

the office of the Litho-carbon Company of New York City.

8. *Kentucky Asphaltic Rock.*—Obtained from Marshall Morris, Esq., Louisville, Ky.

9. *An Asphaltic Mineral.*—Resembling Gilsonite; reported as coming from Utah.

10. *California Maltha.*—Taken from a well at Summerland, on the coast, near Santa Barbara.

11. *Asphaltum.*—From mines recently opened near Asphalto, Kern County, California, in the eastern foot hills of the Coast Range Mountains, about thirty miles west of Bakersfield.

12. *Asphaltic Sandstone.*—From San Luis, Obispo County, California.

13. *Asphaltum.*—Picked up on the beach at San Buen Ventura, California, washed in from the Santa Barbara channel.

14. *Asphaltum.*—From the Ojai ranch, Ventura County, California.

15. *Grahamite.*—A so-called asphaltum taken from a vein in Ritchie County, West Virginia.

16. A portion of a compressed brick made from the asphaltic rock taken from the Seyssel mines. Exhibited at the Columbian Exposition.

17. *Hard Artificial Asphalt.*—An asphaltic residue obtained from the distillation of petroleum obtained near Santa Paula, California. It is known in the refinery of the Union Oil Company, of California, as grade "B."

18. *Soft Artificial Asphalt.*—From the refinery of the Union Oil Company, of California, at Santa Paula. Grade "D."

19. *Asphaltic Pavement.*—Obtained from Franklin Avenue, Buffalo, N. Y. It was laid in 1878, of Trinidad asphalt, wax tailings, and very fine sand. It is remarkable as having been laid for fifteen years with almost no need of repairs.

20. *Asphaltic Pavement.*—From Governor's Island, New York Harbor, laid within the Fort at an unknown date, but so old that it has begun to break up from natural causes. Obtained from J. A. W. Pine, of New York City.

21. *Dubb's Artificial Asphalt.*—A so-called asphaltum obtained in operating the Dubb's patent process for the manufacture of asphaltum by adding sulphur to hot Lima tar and thereby burn-

ing out the hydrogen. This is an asphalt only in name. The specimen was obtained from J. A. W. Pine, of New York City.

22. *Roofing Pitch.*—Obtained from the Mica-asphalt Company, of New York City.

23. *Pitch.*—Obtained as a residuum in the distillation of Scotch blast-furnace tar. This specimen was obtained from the same source as Nos. 20 and 21.

In making tests to determine the best method to be used in the analysis of asphalts the well-known Trinidad and Cuban asphalts were used and all analyses were made in duplicate. In the case of asphalts rich in bituminous matter about a half gram of the material, finely powdered, was used but in the case of asphalts in which the mineral matter constituted a large proportion the quantity was increased to several grams.

The sample was weighed in an Erlenmeyer flask and digested over night in about fifty cc. of petroleum ether; in the morning the clear solution, containing the dissolved petrolene, was passed through a balanced filter and a fresh portion of petroleum ether added to the contents of the flask. The second digestion was continued for two or three hours when the solution, as before, was filtered off and the process repeated until the whole of the petrolene had been removed. The contents of the flask were then thrown upon the filter and thoroughly washed with petroleum ether. Cold turpentine was then poured upon the filter in successive portions until the filtrate passed through colorless when the assumption was made that all the asphaltene and consequently all the bituminous matter had been removed.

The remaining organic matter, not bituminous, was determined by difference, that is, the residue on the filter, after digestion in turpentine, was washed with ethyl alcohol, dried, and weighed in order to determine the percentage of asphaltene after which the residue was burned in a platinum crucible, the difference in weight representing the organic matter not bituminous.

The contents of the crucible were now purely inorganic and, in the case of most asphalts, the residuum was sand more or less colored with iron.

The analysis of Trinidad asphalt under this treatment gave so low a percentage of asphaltene and so large a proportion of

organic matter not bitumen, that it was clearly evident that *cold* turpentine had not dissolved, and could not dissolve all of the asphaltene.

A second set of experiments was then tried in which cold turpentine and carbon disulphide were used as solvents of asphaltene. The results obtained for samples 1 and 2 were as follows:

Sample.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	32.54	20.3435	12.368	34.6775	99.929
" 2.....	25.049	54.53	2.441	17.9215	99.9415

The experiment was now made of somewhat varying the method of treatment for the following reasons: First, because of the difficulty of dissolving out the asphaltene while on the filter by simply allowing the solvent to run through it, and secondly, because, in consequence of the high specific gravity of petroleum ether, a considerable portion of sand or other mineral matter, mixed with asphaltene, always adhered to the flask, thus necessitating a separate determination of this portion. The method now employed for the removal of petrolene and asphaltene was the decantation method, and the solvents used for asphaltene were hot turpentine and chloroform.

The samples were digested over night in petroleum ether; in the morning the solution containing the petrolene was, as far as practicable, removed from the flask and the remainder was evaporated over a steam-bath; after weighing, the residuum containing the asphaltene was digested in hot turpentine over the steam-bath, and finally, the whole contents of the flask were poured upon a balanced filter and treated as in the first experiments.

The percentage composition of Nos. 1, 2, and 17, as determined by the decantation method, was as shown in the following table:

Sample.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	31.51	22.9865	11.4195	34.073	99.989
" 2.....	25.055	52.245	5.758	16.918	99.962
" 17.....	64.571	21.2545	13.706	0.3613	99.8928

In carrying out this method a great many determinations were lost, due to the fact that, in evaporation to dryness over the steam-bath, the contents of the flask were in part bumped out. In consequence, this method was soon abandoned as impractica-

ble, and finally, funnels with stop-cocks were employed, in which the contents of the filter could be digested. Boiling hot instead of cold turpentine was used, and, when necessary, the digestion was continued over night, and all the after washings were made with hot turpentine. Numerous trials showed that carbon disulphide dissolves little more than hot turpentine. The last trace of asphaltene, insoluble in either turpentine or carbon disulphide, was removed by chloroform.

In order to determine the relative solvent power of hot turpentine, carbon disulphide, and chloroform, the following method of qualitative analysis was applied to the twenty-three samples enumerated above. From a half gram to one gram of the material was digested over night in a four-ounce Erlenmeyer flask with about fifty cc. of petroleum ether. Next morning the contents of the flask were poured upon a filter, and the undissolved residue washed with petroleum ether until the filtrate was no longer colored. Boiling spirits of turpentine was then poured upon the filter until it passed through colorless, when carbon disulphide was used in the same manner, followed lastly by chloroform. The action of the successive solvents is shown in the following table:

Sample.	Hot turpentine.	Carbon disulphide.	Chloroform.
No. 1.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 2.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a perceptible amount.
" 3.	Dissolves nearly all.	Dissolves a trace.	Dissolves a trace.
" 4.	" " "	" the slightest trace.	" the slightest trace.
" 5.	" " "	Dissolves a trace.	Dissolves a perceptible amount.
" 6.	" " "	" "	Dissolves a perceptible amount.
" 7.	" " "	" the slightest trace.	Dissolves the slightest trace.
" 8.	" " "	Dissolves the slightest trace.	Dissolves a trace.
" 9.	" nothing.	Dissolves nothing.	" "
" 10.	" nearly all.	" a trace.	" a perceptible amount.
" 11.	" " "	" "	Dissolves a perceptible amount.

Sample.	Hot turpentine.	Carbon disulphide.	Chloroform.
No. 12.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 13.	" " "	" "	Dissolves a perceptible amount.
" 14.	" " "	" "	Dissolves a perceptible amount.
" 15.	" a large amount.	" a considerable amount.	Dissolves a considerable amount.
" 16.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 17.	" a large amount.	" a considerable amount.	Dissolves a considerable amount.
" 18.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
" 19.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 20.	" " "	" "	Dissolves a perceptible amount.
" 21.	" " "	" "	Dissolves a trace.
" 22.	" a large amount.	" a considerable amount.	" "
" 23.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.

Of the twenty-three asphalts examined, there was not one that did not yield some asphaltene on treatment with chloroform; consequently, it is safe to infer that in the analysis of asphalts, unless final washing be made with chloroform, the per cent. of asphaltene will be too low. There was a marked difference observed in the different asphalts as to the manner in which their constituent asphaltene was dissolved on treatment with hot turpentine. In Nos. 4, 5, 6, and 7, and a few others, the asphaltene dissolved out in a few minutes, while in the case of others, notably No. 15, it was a matter of hours, and even of days, before every trace soluble in turpentine could be removed. No. 9 seems to be an asphaltic freak as it contains no petrolene whatever and is insoluble in both hot turpentine and carbon disulphide, while chloroform and amylic alcohol dissolve but the slightest trace.

It was a difficult matter to determine the relative quantity of asphaltene dissolved by the different menstrua, as the only guide used was the color of the filtrate. This suggests a most

interesting research—the fractional, quantitative determination of asphaltene.

From my experience in the analysis of asphalts, I would advise that a preliminary qualitative analysis be always made of each new variety of asphaltum before any quantitative determinations are attempted, care being taken to observe the behavior of different asphalts with the different solvents. This method of procedure is to be recommended, not only because it would prove an economy of time and reagents used, but also because, in this way, much would be learned concerning the nature of petrolene and asphaltene.

A trial was made with Cuban asphalt to determine the solvent power of petroleum ether (87° Beaumé) as compared with that of California naphtha (74° Beaumé) and ethyl ether with the following results:

Sample.	Solvent for petrolene.	Per cent. of petrolene.
No. 2.	Petroleum ether	25.8516
" "	California naphtha	32.444
" "	Ethyl ether	32.5455

The high percentage of petrolene when California naphtha or ethyl ether are used indicates that the asphaltene is, in part, dissolved, and consequently, that these menstrua can not be used as solvents of petrolene in the determination of asphalts.

In selecting a method for the quantitative analysis based upon the results of these experiments, it is assumed that, until a strictly scientific method is worked out, the present empirical determination of petrolene and asphaltene will continue in use. The three considerations of economy, speed, and convenience, will together control the selection. So long as the significance of the difference between the 25.8 per cent. dissolved by petroleum ether and the 32.5 per cent. dissolved by ethyl ether is an unknown element in the problem—that is, whether it be seven per cent. of petrolene or of asphaltene that is involved—it is better to use petroleum ether, because it is cheap and easily obtained of a uniform quality. So, too, it is better to use boiling hot turpentine followed by chloroform as solvents of asphaltene, and thus rid ourselves of carbon disulphide altogether.

With these considerations in view the following method of analysis is recommended:

Weigh two suitable portions in four-ounce Erlenmeyer flasks, add fifty cc. of petroleum ether, cover, and allow to stand over night. The following morning decant the liquid upon a balanced filter placed within a three-inch funnel provided with a stop-cock in the neck. Add another portion of petroleum ether to the flask, allowing two or three hours for digestion, and decant the liquid upon the same filter as before; this process is to be continued until the liquid ceases to be colored, then transfer the whole of the bitumen to the filter. Dry the flask in a steam-bath and weigh; any increase in weight of the flask should be subtracted from the amount determined as petrolene. Wash the filter and its contents with petroleum ether, place these with the filter counterpoise in a steam-bath, dry, and weigh; the loss in weight of the bitumen represents the petrolene.

Rinse the flask thoroughly with boiling turpentine and add the liquid to the filter in the closed funnel, pour upon the filter a sufficient quantity of boiling turpentine to wholly submerge it, cover and allow the digestion to continue for several hours or over night. Repeat the digesting and filtering with boiling turpentine until the filtrate becomes colorless. The filter should be much smaller than the funnel. Rinse the flask with chloroform and pour upon the filter, add sufficient chloroform to wholly submerge the filter and allow at least an hour for digestion; wash with chloroform until the filtrate passes through colorless, then dry and weigh; the loss in weight represents the asphaltene. The filter is now to be burned in a platinum crucible and, if the asphaltum be combined with limestone, the residue recarbonated with ammonium carbonate, dried in a steam-bath, and weighed, the loss in weight represents the organic matter not bitumen, or coke, in the case of artificial asphaltic residuum, produced by heat.

There is necessity for washing the flask with the different solvents, not only because the petroleum ether is too light to rinse out all of the mineral matter, but also because some of the asphaltene adheres to the flask. Generally the turpentine removes all of the mineral matter, as well as part of the asphaltene, but if it does not, then after the flask is rinsed with chloroform it must be again dried and weighed and the increase in weight added to

the weight of the mineral matter in the platinum crucible. If water be present the asphalt should be dried in a steam-bath to a constant weight before being digested in petroleum ether. It is possible that some natural asphalts might experience a trifling loss of volatile oils at the temperature of the steam-bath, but in most instances such loss would be too slight to be regarded. With care and patience this method has been found capable of yielding very closely concordant duplicate results at each step.

The following table exhibits the results of a number of quantitative analyses made according to this method.

Sample.	Water.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	2.029	32.4455	22.1115	8.1215	35.2865	99.994
" 2.....	0.3911	25.4605	54.414	2.469	17.0305	99.7651
" 4.....	....	35.087	63.183	1.7285	.....	99.9985
				Not recarbonated.		
" 5.....	....	8.518	3.924	25.791	61.764	99.997
" 6.....	....	7.486	4.316	.....	88.198	100.
" 7.....	....	8.786	3.267	.....	87.947	100.
" 8.....	....	3.349	2.4215	.....	94.228	99.9985
" 12.....	0.335	11.323	3.81	1.124	83.407	99.999
" 15.....	....	49.959	50.041	.....	.....	100.
" 17.....	....	64.571	21.2545	13.706	0.3613	99.8928
" 18.....	....	63.498	29.966	6.095	.....	99.559
" 19.....	....	4.387	2.831	4.102	88.65	99.97
" 20.....	0.434	6.666	1.87	3.697	87.33	99.997
" 21.....	....	66.788	31.932	1.278	.....	99.998

While this research is in no sense complete—it has in fact but opened up a wide field for further work—yet, sufficient evidence has been obtained to show that petrolene and asphaltene are not substances, but empirical terms that designate mixtures of substances soluble under certain conditions in different menstrua.

It is not unfair to assume that in these empirical mixtures, so long known under the names of petrolene and asphaltene, the lower members of all the different groups of hydrocarbons now known may be found. Again—just as some petroleums, which are varieties of bitumen, consist chiefly of paraffines—notably Pennsylvania petroleum—and some, like Russian petroleum, consist of the additive benzenes, while still others contain mixtures of the two, is it not reasonable to presume that solid bitumens, like liquid bitumens, are equally variable in composition?

If this be the case, then it is equally fair to assume that any solvent taken will not dissolve substances of identical composition from different asphalts.

A review of the results here given suggests the query, have the methods heretofore employed for the technical analysis of asphaltum really been analytical at all? Would not a method and process suggested by the results of the qualitative analyses given in this paper and based on the successive application of different solvents and yielding results similar to those of fractional distillation really become analytical, especially if the separate portions dissolved by the different solvents were subjected to such treatment by oxidizing agents as would enable us by a comparison of the products of oxidation to determine to what groups of hydrocarbons the different substances dissolved respectively belong?

I take pleasure in hereby acknowledging my indebtedness to the courtesy of Hon. Thos. R. Bard, President of the Union Oil Co., of California, for the use of the laboratory of the company while engaged in this research.

MINNEAPOLIS, MINN., Sept. 16, 1894.

ACTION OF METALLIC MAGNESIUM UPON MANGANOUS SALTS.

BY JOS. G. HIBBS AND EDGAR F. SMITH.

Received June 18, 1894.

THE statements relating to the action of metallic magnesium upon solutions of manganous salts are contradictory; thus Manck (Ueber d. Verh. d. Magnesium und Aluminum gegen Salzlösungen, Goettingen, *1862*) states that metallic manganese is readily precipitated by magnesium from neutral solutions of manganous nitrate or chloride. Phipson (*Jahresb.*, *1864*, 192) corroborates this and remarks that the manganese separates as a regulus. The observations of Roussin (*Jahresb.*, *1866*, 170), Comaille (*Comptes Rendus*, **63**, 556; *Jahresb.*, *1866*, 171), and Kern (*Chem. News*, **33**, 236), on the other hand, seem to demonstrate that metallic manganese is not thrown out of manganous salts by metallic magnesium.

We have tried the action of the last metal on manganous salt solutions, both in the presence of alcohol and ether. In using

these liquids, our aim was to reduce the liability of oxidation of manganese, if any should appear, to a minimum.

Experiment 1.—In this trial magnesium acted upon aqueous manganous chloride in the presence of alcohol for a period of two hours. At the expiration of this time the liquid was distilled off, and the material remaining was then carefully analyzed. 0.2582 gram substance was used for this purpose. It showed the presence of 0.0284 gram of chlorine, 0.1392 gram of magnesium, and 0.0539 gram of manganese, or a total of 0.2215 gram.

Experiment 2.—In this, both ether and alcohol were added to the solution upon which the magnesium acted. After removal of the liquids the residue was dried in an atmosphere of nitrogen. 0.6530 gram of it showed the presence of 0.0993 gram of chlorine, 0.3059 gram of magnesium, and 0.1865 gram of manganese, or a total of 0.5917 gram. The action of the magnesium in this instance was only continued through one and a half hours.

Experiment 3.—The conditions here were practically the same as those in experiment 2. The substance was dried, as there, in an atmosphere of nitrogen. Upon analyzing 0.7120 gram of the dry residue it revealed the presence of 0.2302 gram of chlorine, 0.2339 gram of magnesium, and 0.1779 gram of manganese.

In these three trials, as in others which were made, the sum total of the constituents of the reaction product, obtained by analysis, is less than the quantity of material taken for analysis, indicating that, in all probability, it is not metallic manganese which is precipitated by magnesium, but rather, a hydrated oxide, as was suggested by Kern, who used a saturated solution of manganous chloride, and allowed metallic magnesium to act upon it for a period of six to eight hours, with this result:

$$3MnCl_2 + 3Mg + 3H_2O = 3MnO + 3MgCl_2 + 3H_2,$$

and in the presence of water the manganous oxide passes into the protosesquioxide.

Metallic manganese thrown out by the electric current, oxidizes rapidly on momentary contact with the air, and even if it should come down as metal, through the action of magnesium, it is scarcely probable that, in the finely divided state in which it would be, it could long resist the action of the surrounding water.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

NOTE ON THE TEST FOR STRYCHNINE.[1]

By W. P. Mason and J. W. Bowman.

ORGANIC matter having been removed, and the solution containing the purified alkaloid having been evaporated to dryness on the water-bath, the dry residue is taken up with a little concentrated sulphuric acid, one of several oxidizing agents added in solid form, and the well-known strychnine color reaction forthwith appears as usual. Or, in the event of the evaporation having been accomplished in a platinum dish, such dish may be connected with the positive pole of a battery, and, upon touching the negative pole to the acid contents, the strychnine color instantly flashes out. All this being long since known, the following table is offered to indicate the relative degrees of delicacy of the several reagents commonly employed.

In each instance the figures at the top indicate the number of milligrams of strychnine sulphate actually operated upon, *i. e.*, the amount left upon the evaporating dish by the evaporation of the measured quantity of standard solution employed.

Amount used in milligrams.	0.500	0.400	0.300	0.250	0.150
$K_2Mn_2O_8$ ...	very strong	very strong	very strong	very strong	strong
$K_2Cr_2O_7$	very strong	very strong	very strong	very strong	strong
PbO_2.....	fair	fair	weak	no test	no test
$K_6Fe_2(CN)_{12}$	strong	strong	strong	strong	strong
MnO_2	strong	strong	strong	strong	strong
H_2CrO_4.....	very strong	very strong	very strong	strong	strong
Battery	strong	fair	no test	no test	no test

Amount used in milligrams.	0.050	0.025	0.020	0.015	0.010
$K_2Mn_2O_8$ ...	strong	strong	weak	very weak	no test
$K_2Cr_2O_7$	fair	weak	very weak	no test	no test
PbO_2.....	no test	no test	no test	no test	no test
$K_6Fe_2(CN)_{12}$	fair	fair	weak	very weak	no test
MnO_2	strong	fair	weak	weak	very weak
H_2CrO_4.....	weak	no test	no test	no test	no test
Battery	no test	no test	no test	no test	no test

From the foregoing it will be seen that beautiful as Letheby's galvanic test is, it does not compare favorably in point of deli-

[1] Read at the Brooklyn Meeting, August 16, 1894.

cacy with the more common ones using chemical reagents It certainly fails long before the bitter taste disappears.

From the table it would seem that MnO_2 should be given the first rank, but the slowness of its action is greatly in its disfavor, and the consequent difficulty of getting the color to flow down the side of the dish from the crystal of reagent is an objection. The presence of a little organic matter, also masks its action.

Altogether, we found that $K_2Mn_2O_8$ gave the most satisfactory results. Of course, the color of this reagent is an argument against its use, but if the acid used be of full concentration, and if a blank experiment be run at the same time with acid only in the dish, no trouble need be feared from that source.

RENSSELAER POLYTECHNIC INSTITUTE,
June 4, 1894.

THE DETERMINATION OF MELTING-POINTS AND THE COMPOSITION OF SOME CANDLE MATERIAL.

BY W. E. GARRIGUES.

Received October 15, 1894.

THE so-called melting-point of a fatty substance is obtained in such a variety of ways, and with equally varied results, that the claim of a certain figure for any particular article of commerce is really of little or no value, unless accompanied by a description of the method employed in its determination, which for ordinary trade conditions is hardly feasible.

There is probably no method in common use, even comparatively independent of personal equations and respective laboratory conditions. Those proposed for determining melting-points in capillary tubes etc., besides being open to these objections, necessitate allowing the fat to harden for many hours before applying the test. Wiley's method for butter fat is both tedious and difficult of manipulation and of course useless for free fatty acids.

The solidifying point, after Dalican, is not infrequently reported as the melting-point of stearic acid candles, and would if this were the only material employed, be an easy and fairly good solution of the problem; obviously, however, it is valueless for paraffin-wax and even for many mixtures of the two. The writer believes that any procedure which will quickly give

results on all kinds of candle material, the figures capable of being checked by different manipulators, is a much felt want among chemists engaged in such work.

In American oil refineries the melting-point of paraffin is usually determined by immersing the bulb of the thermometer to two-thirds its length in the molten wax, which is then permitted to cool slowly until the first signs of incipient solidification appear on the surface, disregarding that portion in immediate contact with the sides of the dish. The height of the mercury is then read off.

In some works this is slightly varied by drawing the point of a pin across the surface of the melted wax, until a "string" of the latter can be picked up. This is regarded as the melting-point.

A modification of Dalican's method, seemingly capable of universal application to substances solid at ordinary temperatures, was some time ago called to the writer's attention by Mr. Thomas S. Gladding. It consists of observing the temperature at which a fatty substance solidifies while in constant agitation.

The process is conducted by Mr. Gladding in the following manner: Thirty to fifty cc. of the dried sample is placed in a small beaker, the bulb of the thermometer is completely immersed therein and the glass with its contents twirled continuously in one direction until the mercury stops receding or ascending.

At first it falls rapidly and regularly but its subsequent behavior varies with the nature of the substance under examination. With fatty acids there is a rise of from 0.1° to 1° C., averaging about 0.3° for commercial stearic acid; here it remains stationary for about one minute. With paraffin-wax no rise results, but the mercury remains stationary about one-half minute and then continues to recede at the rate of 0.1° to 0.2° per minute. The fall prior to reaching this point being much swifter, no difficulty is experienced in noting the exact temperature. With mixtures of stearic acid and paraffin there is great diversity, the observed figures ranging from no rise, to one of nearly 4°. The latter representing a mixture of two-thirds stearic to one third wax.

Following is a table showing this melting-point of such mix-

tures in different proportions. The last column gives the action of the mercury at the time of solidification:

	Stearic.	Paraffin.	Melts at	
1	100	0	54.6	0.1 rise.
2	100	10	53.4	No "
3	100	20	52.4	" "
4	100	30	51.6	" "
5	100	40	50.8	0.05 "
6	100	50	50.1	0.2 "
7	100	60	49.2	0.6 "
8	100	70	48.2	0.8 "
9	100	80	47.4	2.8 "
10	100	90	45.6	0.6 "
11	100	100	45.2	0.8 "
12	90	100	45.8	No "
13	80	100	46.3	" "
14	70	100	46.9	" "
15	60	100	47.3	" "
16	50	100	47.9	" "
17	40	100	48.6	" "
18	30	100	48.9	" "
19	20	100	49.6	" "
20	10	100	50.4	" "
21	0	100	50.8	" "

To check No. 9, the same paraffin was mixed with another sample of stearic and gave:

Stearic.	Paraffin.	Melts at	
100	0	53.1	0.6 rise.
100	20	50.8	0.6 "
100	40	49.0	0.7 "
100	60	46.5	3.6 "
100	80	45.9	3.1 "

NOTE.—These tables were constructed with a view to practical uses, hence, the proportions, as above, instead of even percentages reckoned on the mixture. In candle factories the predominant material is taken as a basis of calculation. Thus, forty per cent paraffin means 100 parts stearic acid to forty parts wax.

The great advantage claimed for this method is the concordance of its results in different hands. The figures obtained are always the same to 0.1°. The only caution necessary is in cases where apparently no rise of the mercury will take place; the twirling motion should be continued until the mass assumes an unbroken white color and a homogeneous semi-solid consistency. This may take some minutes; then if still no rise occurs the temperature at which there was a pause

is to be noted. A few trials with a mixture like No. 9 will make this clear.

The thing to guard against is being deceived by an action of the mercury similar to say No. 15. For several minutes before the enormous rise in the former, it almost stops, sinking no faster than after reaching the true point in the latter. The appearance of the substance under examination is, however, vastly different, being in No. 9, coarse, white flakes floating in a clear molten liquid. On continuing the motion, the mass suddenly blends to a solid white, the temperature rising rapidly; the highest point reached being the melting-point. On paraffin-wax, the refinery test previously mentioned, shows about 0.6° C. higher than Gladding's.

Chemists have for some time been aware that a mixture of fatty acids, subjected to distillation with superheated steam, undergoes some change. It is known that a quantity of liquid hydrocarbons is formed, together with a black pitch; also that there is a slight increment in the melting-point. Alder Wright ascribes this latter to the possible formation of isoleic acid or stearolactone. A limited investigation by the writer, carried on at a large candle works, is felt to be a small grain added to a rather barren fund of literature on this subject.

An oft occurring mistake in connection with published analyses of candle material, is the omission of the details of manufacture. For instance, to give the average composition of commercial stearic acid, means absolutely nothing when we consider that one manufacturer employs palm-oil as a source while another uses tallow or bone-fat. A third both saponifies and distills with steam while a fourth uses sulphuric acid or presses the fatty acids directly without distillation. It therefore becomes essential to preface any report of this kind with a brief outline of the several stages through which the fatty substances pass.

The fats under consideration here are exclusively tallow and bone-fat. These are saponified in an autoclave under 150 pounds steam pressure and without the aid of any base. All that is of sufficiently good color is then at once subjected to pressure at ordinary temperature, followed by a second hydraulic pressing, at steam heat. The solid cake of fatty acids thus obtained,

needs only to be freed from dirt before being ready for the candle-molds. The oil expressed hot is permitted to chill, re-pressed cold, and the solid residue again subjected to the hot pressing. This is continuous, the cake from the hot press alone being used in the molding room.

The dark fatty acids, from the autoclave, before receiving the above treatment, are subjected to distillation, in copper, with superheated steam; 16,000 to 18,000 pounds constituting one "run," during which the volume in the still is kept constant by a continuous inflow from the storage tank above.

The distillate is caught in three fractions. The white oil, comprising about four-fifths of the whole is obtained first. This we will call "first run oil;" it is ready for pressing at once. The hydrocarbons that are formed having, in part at least, a higher boiling-point than the fatty acids, accumulate in the still and when these begin to come over in quantity sufficient to color the distillate a decided green, the receptacle is changed. What now comes over we will term "second run oil;" it is returned to the storage tank and redistilled with the next run.

After a time the distillate again changes color becoming darker and more viscid. The operation is then stopped and the contents of the still permitted to cool, subsequently being transferred to a smaller iron still in which a higher heat can be attained. The fraction obtained here we will designate "green oil." There now remains as a residue a black pitch, called "candle tar."

As will be seen later, from its analysis, the practice of returning this green oil to the storage tank, for redistillation with other fatty acids, can not be looked upon in any other light than as an adulteration of the red oils, finally obtained, into which it finds its way.

Going back to the autoclave we find little of interest except perhaps the degree of perfection attained by this mode of saponifying, without any base. Samples removed after ten, twelve, and fourteen hours digestion, showed respectively 1.74, 1.44, 1.06 per cent. glycerol.

NOTE.—The unsaponified fat may be approximately deduced on multiplying these figures by ten.

As might be expected, no change occurred in the constitution of the fat, other than the removal of glycerol. Facilities for trying the effect of higher pressure than 150 pounds were lacking.

Proceeding to the distillation, we find the following changes take place:

BEFORE DISTILLATION.		AFTER DISTILLATION.	
Melting-point.	Per cent. oleic acid.[1]	Melting-point.	Per cent. oleic acid.
41.5	43.96	44.5	35.06
43.6	44.64	45.5	36.06
43.9	41.67	45.0	34.00

These melting-points are lower than those of the pure fatty acids alone; due in the first column to the presence of neutral glycerides, to the extent of ten to fifteen per cent., and to hydrocarbons from a previous distillation, as before mentioned. Distillation almost eliminates the former, but the hydrocarbons are still there in about the same proportion (*vide infra*).

To determine quantitatively the changes wrought by the high temperature, about 260° C., a run of 16,075 pounds was traced through, and the chemical composition before and after noted, as well as the proportion of the different grades of oil previously named. These figures may be taken as typical, the variation from averages being very small.

The oil had a melting-point of 43.2° C. and contained:

	Before distillation, per cent.	After distillation, per cent.
Solid acids	49.52	50.47
Oleic acid	42.86	33.05
Hydrocarbons (liquid)	6.94	13.14
Glycerol[2]	1.37	....
Tar	....	2.00
Loss	....	1.34
	100.69	100.00

The percentage yield of the different grades of oil and the constitution of each was:

[1] NOTE.—All the percentages of oleic acid given in this paper were obtained by calculation from the iodine absorption figure. The melting-points are those described in the beginning of this article.

[2] NOTE.—One-half the glycerol found is subtracted, together with oleic acid and hydrocarbons, from 100 to determine the solid acids, since tallow glycerides yield approximately ninety-five per cent. fatty acids and ten per cent. glycerol.

First run oil....	80.31	Containing:	Hydrocarbon...	6.29 per cent.
Melting-point 44.8			Fatty acids	93.71 "
Second run oil..	12.13	Containing:	Hydrocarbon...	35.90 "
			Fatty acids	64.10 "
Green oil.....	4.22	Containing:	Hydrocarbon...	98.74 "
Tar.....	2.00		Fatty acids	1.26 "
Loss.....	1.34			
	100.00			

Making corrections for the hydrocarbons present before distillation and the glycerol, which forms a large part of the 1.34 per cent. loss, we have as a result of distilling 100 parts of pure fatty acids:

	Before.	After.
Solid acids.....	53.61	54.63
Oleic acid.....	46.39	35.77
Hydrocarbons (liquid).....	....	6.71
Tar.....	....	2.15
Loss.....	....	0.74
	100.00	100.00

It seems reasonably assured, from these figures, that the stearic and palmitic acids distill without change, while the oleic partly splits up into liquid hydrocarbons, tar, and a saturated or non-iodine consuming fatty acid. The nature of this body, though it has not been isolated, will be considered briefly farther on.

From the foregoing facts, it appears to the writer that the present process of manufacture might be advantageously altered by taking the fatty acids directly from the autoclave to the presses—as is done with the light colored stock—and obtaining a press-cake melting at 55°–56°, which latter is then subjected to distillation. By these means the candle stock would not deteriorate in the still as it now does (*vide infra*), and the formation of valueless—and even for most purposes harmful—hydrocarbons would be avoided, giving the red oils a greater worth.

Practical candle makers find that distilled stock invariably yields a press-cake of lower melting-point than that from the autoclave. This is now explained by the formation of the saturated fatty acid from oleic acid, in the still. This body is sufficiently solid to resist being pressed out with the oleic acid, yet

soft enough to lower the melting-point of its associates—stearic and palmitic.

NOTE.—As shown by several writers, the lowering of the melting-point of a mixture of two fatty acids by the addition of a third, does not necessitate the latter having a melting-point below that of the two former.

Apart from the evidence already given its presence is indicated by its low molecular weight, being—probably considerably—under 268, while the mean of stearic and palmitic as occurring in tallow is 271–272. The following tabulated analyses of press-cakes in different stages of completion, illustrate these points.

	AUTOCLAVE STOCK.				STILL STOCK.		
	Melting-point, 0° C.	Per cent. oleic acid.	Total mean equivalent.	Molecular weight of solid acids.	Per cent. oleic acid.	Total mean equivalent.	Molecular weight of solid acids.
1....	51.0	....	....	....	16.69	....	....
2....	51.5	21.08	....	....	....	....	....
3....	53.6	....	....	....	7.02	....	....
4....	53.8	11.57	....	....	....	....	....
5....	54.1	9.00	....	....	....	....	....
6....	54.3	....	....	....	6.51	269.2	268.3
7....	54.4	8.40	....	....	5.51	269.2	268.4
8....	54.5	....	....	....	5.96	268.4	267.5
9....	54.6	....	....	....	6.00	268.0	267.0
10....	54.8	....	....	....	4.99	268.4	267.6
11....	54.9	6.60	272.0	271.2	4.16	270.0	268.4
12....	55.5	4.37	....	....	....	....	....
13....	55.6	4.02	272.0	271.5	....	....	....
14....	56.0	3.74	272.8	272.4	....	....	....
15....	56.1	3.96	272.0	271.5	....	....	....
16....	56.2	3.03	....	....	....	....	...

NOTE.—The average content of neutral glycerides was determined to be 3.90 per cent. in samples 11, 13, 14, 15, from the autoclave, which is offset by an average of 0.17 per cent. hydrocarbons in samples 6 to 11, inclusive, from the still. In calculating the mean equivalents, no corrections were made for these in either case. The method of determination was; boiling with an excess of alcoholic potash and back titrating.

To sum up, in conclusion, it appears that when oleic acid is distilled in an atmosphere of steam, the distillate contains, besides unaltered oleic acid, hydrocarbons—liquid, and mainly of high boiling-point—and one or more fatty acids, not isomerides of oleic, having a considerably higher melting-point and lower mean equivalent than the latter, and differing therefrom in not forming addition products with iodine. A black pitch remains as a residue in the still.

SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.[1]

By H. F. Keller.

IN the extraction of metals from their oxygen compounds, carbon is certainly the most important and useful reducing agent. Its great affinity for oxygen is utilized in the manufacture of iron and steel; the commercial production of other useful metals, such as copper, lead, zinc, and tin is accomplished, either directly or indirectly, with its aid; and under its influence even the energetic metals of the alkalies release their powerful grip upon oxygen. Contrasted with this, the use of other substances for the purpose of abstracting oxygen is almost insignificant. Is it surprising, therefore, that carbon is looked upon as the reducing agent *par excellence*, or that the very idea of reduction seems to us inseparably associated with this element?

But the reducing power of a substance depends, in a large measure, upon temperature. It is well known to chemists that, under certain conditions, many metals have affinities which are far more powerful than those of carbon. When we glance over the pages of our chemical text-books, we see described there numerous experiments based upon the superior combining power of iron, aluminum, zinc, magnesium, and the alkali metals. The great Swedish chemist who arranged the elements according to their supposed affinities in an electro-chemical series, was among the first to employ the positive alkali metals for isolating and preparing other elements. His method consisted in decomposing the halogen compounds by means of potassium; and it was subsequently improved by Berzelius' distinguished disciple, Wöhler. With its aid, the latter chemist not only succeeded in reducing for the first time those remarkable metals, aluminum and glucinum, but he also showed that *all* those metals, the oxides of which cannot be reduced by either carbon or hydrogen, may be obtained by the action of potassium upon their halogen compounds.

It must not be supposed, however, that the use of metals as reducing agents is confined to the laboratory and the lecture

[1] First published in the Journal of the Franklin Institute, October, 1894.

table. Practical applications of such reactions may be less conspicuous, but they constitute, nevertheless, the basis of not a few important metallurgical processes. The "precipitation" of lead from its sulphide ores; the solution of silver by the nascent lead in the blast-furnace; the amalgamation of the same metal in the iron pan; Deville's process of extracting "silver out of clay," recently so greatly perfected by Castner and Netto—are they not essentially reductions by means of metals?

In view of the facts mentioned, it may appear strange that comparatively little progress was made for many years in the study of the reducing properties of metals. We can, however, satisfactorily account for this when we consider the great tendency of metals to form alloys; it is difficult, in many cases indeed impossible, to obtain products entirely free from the reducing metal, and it is also well known that even a trifling amount of such an impurity may seriously impair the valuable qualities of a metal. Another obstacle has been the high price of those metals, which, by reason of their more powerful affinities, could, with advantage, be substituted for carbon.

Recent improvements in the commercial production of some of these metals have partially removed the latter obstacle. Thanks to the rapid progress of electro-metallurgy, aluminum is now to be had for about half a dollar per pound; sodium, once a chemical curiosity, is manufactured on an enormous scale at a less cost even than aluminum; and magnesium, now successfully extracted from carnallite, is applied to a variety of technical uses.

The radical changes which have taken place in our views on chemical affinity, as a result of the study of thermo-chemical phenomena, and the theory that the properties of the elements are *periodic functions* of their atomic weights, have also largely contributed to awaken interest and activity in the subject of our discussion.

The remarkably high heats of formation of its oxide and chloride, as well as the great stability of these compounds, render the action of magnesium upon other oxides and chlorides particularly interesting. Clemens Winkler, of Freiberg, has presented us with a most careful and systematic investigation of

the reducing action of this metal upon oxides, while Seubert and Schmidt have communicated a similar exhaustive study of its action upon chlorides.

In giving a brief résumé of the results obtained by these experimenters, I shall adhere to the order adopted by them. It is based upon the periodic system, and has the advantage of showing many interesting relations that might otherwise escape notice.

GROUP I.

Group I embraces a main group consisting of lithium, sodium, potassium, rubidium, and cesium, and a sub-group consisting of copper, silver, and gold.

Owing to the difficulty of obtaining the oxides of the alkali metals in a pure condition, the carbonates were employed. It was found that to insure the best results three atoms of magnesium are required for every molecule of the carbonate, thus: $Na_2CO_3 + 3Mg = 3MgO + C + 2Na$.

The carbon as well as the sodium are deprived of their oxygen. It was found that, with the exception of cesium carbonate, the alkaline carbonates *suffer reduction* to the metallic state when heated with magnesium, but that the intensity of the reaction diminishes as the atomic weight of the metal increases. Lithium, *e. g.*, whose atomic weight is only seven, was reduced with explosive violence, the metal being completely vaporized, while the tube in which the reduction was effected was shattered to pieces; potassium (atomic weight 39), and rubidium (atomic weight 85) on the other hand, were reduced quickly and without notable vaporization.

The reduction may be made in a tube of hard glass closed at one end; it is better observed, however, by conducting it in a current of hydrogen.

The preparation of potassium affords a most instructive experiment, which may well serve for lecture demonstration.

Into a wide tube of Bohemian glass, a porcelain boat, containing about two grams of the mixture of potassium carbonate, and magnesium is introduced. A current of perfectly dry hydrogen gas is passed through the tube, and the part of the tube surrounding the boat is gradually heated to incipient redness;

the mass darkens, and upon further raising the temperature with the aid of the blast-lamp, the reduced potassium is completely expelled from the boat, exhibiting the deep green color of its vapor, and is deposited in the form of a bright mirror in the cooler part of the tube. At the same time the hydrogen flame shows an intense violet color. The dark residue remaining in the boat consists of magnesia and carbon. Enough potassium will have collected to show its color, luster; that it is sectile, fusible; its action upon water, bromine, etc.

In view of the high price of metallic potassium, the question as to whether the described reaction might not be carried out on the large scale suggested itself. Experiments showed, however, that in the absence of a gas current, the distillation of the metal is very incomplete; and inasmuch as carbon monoxide forms an explosive compound with this metal, illuminating gas could not be substituted; in fact, the explosive carbonyl-potassium was invariably formed when the quantity of magnesium present was insufficient for the *complete* reduction of the carbonate.

This was further proved by experiment. When two atoms only of magnesium were taken, the reaction took place according to the equation:

$$CO\begin{matrix}OK\\OK\end{matrix} + 2Mg = CO + 2K + 2MgO.$$

More promising results were obtained by employing potassium hydroxide instead of potassium carbonate. The danger of forming the explosive body is thus avoided, while the hydrogen gas set free simultaneously with the potassium, insures the complete distillation of the latter:

$$KOH + Mg = K + H + MgO.$$

The reaction is somewhat violent, but may be moderated by adding some inert substance, such as magnesia, or by using the magnesium in the form of lumps or bars.

Winkler says "it does not seem unlikely that the manufacture of potassium could be carried out by means of the same apparatus, and the same operations, which C. Netto has so successfully employed in reducing caustic soda with carbon. Into a retort filled with bars of magnesium, and heated to redness, melted potash would be allowed to flow in a continuous stream, while

the escaping mixture of potassium vapor and hydrogen is being cooled."

Winkler figures the cost of a pound of potassium to be about $3.75; the metal is now quoted at $28.

Beketow, who had previously made use of the action of aluminum upon potassium hydroxide, obtained only one-half of the theoretical yield owing to the simultaneous formation of potassium aluminate.

The sub-group, consisting of the heavy metals copper, silver, and gold, exhibited the reverse behavior; the reduction was more energetic the higher the atomic weight of the metal. A very *slight* deflagration accompanied the removal of oxygen from cuprous oxide, while silver oxide was reduced with *explosive violence*. Very curiously aurous oxide was not visibly affected by the magnesium. This is explained, however, by the fact that gold oxide splits up into its constituents considerably below the ignition point of magnesium.

GROUP II.

The main group comprises glucinum, magnesium, calcium, strontium, and barium; and zinc, cadmium, and mercury, constitute the sub-group.

These elements are bivalent, and the action of their oxides upon magnesium is therefore:

$$R'' O + Mg = MgO + R''$$

In some cases the *hydroxides* were also used.

Glucina was easily reduced by magnesium; the mass became slightly incandescent, but some unaltered oxide was found in the residue.

There was no action observed when a mixture of magnesium and magnesia was heated in hydrogen; the oxide remained in the boat, while the metal sublimed in beautiful crystals. The existence of Beetz's suboxide could not be confirmed.

No visible sign of chemical action occurred when lime and magnesium were heated together. The reduction proved nevertheless to be almost complete.

A slight incandescence attended the reduction of strontia, whilst barium oxide displayed an energetic action upon magnesium. In both cases the decomposition was apparently complete.

None of the alkaline earth metals were found to be volatile at the temperature of reduction.

The hydroxides were even more readily acted upon than the oxides; so striking and beautiful, indeed, were the phenomena observed in the cases of calcium hydroxide and strontium hydroxide, that Winkler proposes to utilize them for lecture illustration, and in pyrotechnics.

The reduction of the oxides belonging to the sub-group was very energetic, the resulting metals being vaporized completely. Cadmium oxide develops less energy than either zinc oxide or magnesium oxide.

Both in the main group and the sub-group, the maximum of chemical energy occurs in the second member.

GROUP III.

The main group embraces boron, aluminum, (scandium,) yttrium, lanthanum, and ytterbium, and gallium, indium, and thallium, form the sub-group. Three atoms of magnesium are required to abstract the oxygen from their oxides:

$$R_2O_3 + 3Mg = 3MgO + 2K'''$$

Phipson has observed that boric acid is reduced upon ignition with magnesium. With the aid of magnesium, boron was also obtained by Geuther from the boro-sodium fluoride, and quite recently L. Gattermann has shown that boric acid, as well as borax can be reduced by means of this metal, so as to yield products which are suitable for the preparation of various volatile boron compounds.

Winkler confirmed these observations. He states that the trioxide and the borate of sodium are easily reduced, the latter with much energy and evolution of sodium vapor. But he found that, instead of free boron, the residue contains magnesium boride of variable composition; for, on treatment with hydrochloric acid, boron hydride is given off as a gas. Sometimes a solid residue remains, which is likewise a compound of boron and hydrogen.

Owing to the acid-forming character of boron, the reduction was never complete; borates, upon which magnesium has no action, are always formed.

An attempt was also made to prepare a boron suboxide by limiting the supply of magnesium, thus:

$$B_2O_3 + Mg = 2BO + MgO$$

but no indication of such an oxide was observed.

A dark colored product resulted from heating alumina with magnesium. The reaction appeared to be quite energetic; the mass exhibited a vivid glow and increased largely in volume. In addition to finely divided aluminum, a new oxide, AlO, and magnesium spinel had been formed. This monoxide could not be obtained in a pure condition, but its existence was proved beyond doubt. It is best prepared by heating in a current of hydrogen, a mixture corresponding to

$$Al_2O_3 + Mg = 2AlO + MgO.$$

This oxide is a brownish-black, voluminous powder, is pyrophoric, and liberates hydrogen slowly from water; it precipitates cuprous oxide from copper sulphate solution, and is exceedingly susceptible to oxidation.

Winkler suggests that the blue color of sapphire, and possibly also that of ultramarine, may be due to a small proportion of this monoxide.

Of the rare earths of group III, only yttria and lanthana were subjected to the action of magnesium. The energy of the reduction appeared to increase with the atomic weights.

Upon the oxides of the sub-group, magnesium reacts with great violence; the intensity of reduction has its maximum in In_2O_3.

The behavior of Tl_2O_3 towards magnesium, appears to be an exception. Before the temperature of reduction is reached, this oxide splits up into Tl_2O and O_2, and the thallous oxide so formed is then only partially reduced. Thallium carbonate, however, is deprived of its oxygen completely and with explosive violence.

GROUP IV.

The most interesting results, perhaps, were obtained in the fourth natural group of elements.

The known properties of carbon, silicon, titanium, zirconium, cerium, and thorium, assign them positions in the main group, while germanium, tin, and lead, constitute the sub-group.

In addition to their acid-forming dioxides, the majority of these elements are capable of giving monoxides. It was therefore deemed desirable to attempt not only the complete reduction of the higher oxides, but also a *partial* removal of the oxygen with a view to procure the lower oxides.

The statements of different experimenters concerning the action of carbon dioxide upon magnesium are somewhat conflicting.

That a ribbon of the metal will burn in an atmosphere of carbon dioxide was first observed by Kessler, but neither he nor other chemists who repeated and modified his experiment explained satisfactorily the nature of the reaction.

Winkler shows, in the first place, that magnesium, when *moderately* heated in a current of carbon dioxide, does not take fire, but is slowly converted at its surface into a carbide, carbon monoxide being formed at the same time. Upon increasing the heat to a full redness, the metal was inflamed and continued to burn with a dazzling light. The products of this combustion are magnesia and carbon.

When the magnesium is employed in the form of powder, these reactions take place even more readily. At a temperature considerably below a red heat carbon monoxide appears, and its quantity is greatly increased when low redness is reached. The metal burns with great brilliancy at a full red heat, and unless the current of carbon dioxide is very rapid, its reduction is complete.

It has already been mentioned that a separation of carbon was observed when magnesium acted upon carbonates; also that carbon monoxide was formed when an excess of the carbonate was present. Further experiments were made with calcium carbonate. A mixture of this substance with magnesium: $CaCO_3 + 3Mg = Ca + C + 3MgO$, heated in a current of hydrogen detonated violently. The examination of the débris, revealed the presence of a carbide of magnesium. No metallic calcium was observed in the residue when only two atoms of magnesium were used for each molecule of the carbonate.

According to Kessler, burning magnesium is extinguished in carbon monoxide, while Parkinson asserts that at a red heat the

metal burns vividly in this gas. Both observations were found to be correct. A spiral of magnesium wire ignited in the air, ceased to burn while introduced into a jar of carbon monoxide, but when strongly heated in a current of the gas the magnesium emitted light, and a gray coating of a carbide appeared on its surface.

Numerous experiments to determine the exact composition of this carbide were made, but without yielding a definite result.

Silicon exhibits a pronounced tendency to combine with magnesium. Silicon-magnesium was first observed by Wöhler, in 1858.

The reduction of silica by metallic magnesium was observed in 1864, by Phipson, and Parkinson showed in 1867 that silicon-magnesium, as well as a magnesium silicate, are formed at the same time. A few years ago L. Gattermann published an interesting paper, in which he showed how very easily silicon dioxide is reduced by magnesium. He states that either silicon or silicon-magnesium can be obtained by varying the proportion of magnesium; and he applies the reaction to the preparation of volatile compounds of silicon, such as the chloride, bromide, iodide, silicoformic acid, silico-chloroform, etc.

Gattermann and Winkler agree that an energetic reaction occurs upon heating a mixture of one molecule of silica and two atoms of magnesium.

$$SiO_2 + 2Mg = Si + 2MgO.$$

By adding magnesia to the mixture, the heat of the reaction was moderated, but it was then found that much silicon-magnesium was contained in the product. If the reaction be effected at low temperature and in the presence of an excess of magnesium, silicon-magnesium is always formed, while at a high heat or in presence of magnesium, only amorphous silicon results.

A silicon monoxide could not be obtained by the reduction of silica, either by magnesium or silicon.

Many silicates are reduced quite as easily as the dioxide; in some cases the metallic base is likewise reduced, *e. g.*, potash glass.

None of the oxides studied presented greater difficulties than

titanium dioxide. The results may thus be summed up: Titanium dioxide was not reduced to the metallic state; a mixture of monoxide and a titanium spinel were the products of the reaction. Other intermediate oxides were sometimes formed. When the residue was treated with hydrochloric acid, HTi_3O_4 was formed, which, upon heating, gave TiO_2 and hydrogen. Neither titanium-magnesium, nor a titanium hydride, was observed.

The reduction of zirconia was effected by heating it with magnesium to a high temperature. A monoxide could not be identified with certainty; and $ZrMg_2$ does not appear capable of existing.

According to the amount of magnesium employed either cerium or Ce_2O_3 were obtained from cerium dioxide. An intermediate monoxide was not formed. The reduction begins at a moderate red heat and is accompanied by a vivid glow. A considerable proportion of the magnesium is volatilized. In the nascent state, cerium was found to absorb hydrogen in large quantities.

The formation of a metallic hydride at a bright red heat is a most remarkable observation. It is clearly proved to be correct by the following experiment.

A mixture is prepared according to the equation:

$$CeO_2 + 2Mg = Ce + 2MgO$$

Twenty grams of this mixture are placed in a combustion tube through which a current of dry hydrogen is passed, while a gentle heat is applied to expel any moisture. The further end of the tube is then closed with a strong clip. Hydrogen is allowed to enter the other end and the heat quickly raised to bright redness; a rapid current of hydrogen is seen to pass through the wash-bottles into the tube.

The hydride is of a brownish-red color. It is without action on water at ordinary temperatures, but sets free hydrogen upon heating. Hydrochloric acid dissolves it to $CeCl_3$, with evolution of hydrogen. It was found impossible to completely remove magnesia from the product. The hydride is very inflammable, and detonates with potassium chlorate, potassium nitrate, etc.

The analytical results obtained point to the formula CeH_2.

After the existence of a cerium hydride had thus been established, the thought suggested itself that the other elements of Group IV might possibly be capable of forming similar compounds. Only carbon and silicon were known to form hydrides, but these elements could not be made to unite with hydrogen when their oxides were reduced by magnesium. Since titanium could not be reduced to the metal, it is not strange that all efforts to form a hydride gave negative results; zirconium and thorium did absorb hydrogen and yielded hydrides similar to CeH_2. The same was observed with lanthanum and this led Winkler to believe that this element belongs to the cerium group; but he showed subsequently that yttrium and other trivalent elements, and even the divalent barium, strontium, and calcium can unite with hydrogen.

These hydrides represent a new class of metallic compounds, in which only half the usual valence of the metals is satisfied.

The action of magnesium upon chlorides has been made the subject of an elaborate research by Seubert and Schmidt.

I must content myself with a very brief statement of some of the main results obtained by these chemists.

Both the anhydrous bodies and the aqueous solutions of the chlorides were subjected to the action of magnesium.

In the former case the substance, either mixed with magnesium powder, or conducted over it in the form of vapor, was heated to a high temperature. It was found that all chlorides could thus be reduced to the metallic state, but the reduction was incomplete in the groups of the metals of the alkalies and the metals of the alkaline earths.

In *neutral* aqueous solutions, all the metallic chlorides, save those of the alkalies and those of the alkaline earths, gave up their chlorine to the magnesium. In some cases the metals were deposited in the metallic state, (silver, gold, thallium, lead, arsenic, antimony), but in most cases, hydroxides were precipitated. These hydroxides always represent the lowest state of oxidation. $CuCl_2$, *e.g.*, is changed into Cu_2O; chromium, aluminum, iron, manganese, cobalt and nickel, all yielded hydroxides.

It would seem that the tendency to form such hydroxides is

peculiar to the positive metals, and especially to those forming basic salts. Seubert and Schmidt believed this to be due to a dissociation of the chlorides into hydroxides and hydrochloric acid. They suppose, for instance, that an aqueous solution of $AlCl_3$, contains $Al(OH)_3$, $3HCl$. This view is rendered quite probable by the fact that solutions of copper, nickel, cobalt, and chromium exhibit the color of their *hydrated* salts.

Of other metals whose oxides possess a high heat of formation, aluminum has found some application in the reduction of oxides. Beketow has employed it with success to prepare some of the metals of the alkalies; and the experiments of Greene and Wahl of reducing manganese oxides by means of metallic aluminum are still fresh in our memory.

I am convinced that a continued study of the relative affinities of the metals for oxygen and other negative elements, will lead to important applications in metallurgy, and give new and valuable methods to synthetic and analytical chemistry.

OBSERVATIONS ON AMERICAN OIL OF TURPENTINE.

By J. H. Long.

Received October 24, 1894.

IN the February, 1893, number of the *Journal of Analytical and Applied Chemistry* I called attention to certain peculiarities of our American turpentine-oil as distilled from the crude turpentine produced in the southern states.

It is well known that the chief difference between the so-called French and American turpentines is found in their behavior toward polarized light, the French oil being laevo-rotatory, while that produced here has always been described as dextro-rotatory.

In the course of the examination of a large number of samples distilled in the laboratory from fresh crude turpentine sent me directly, I found that some disclosed a very low rotation, and a few were even laevo-rotatory. Through the courtesy of Mr. E. B. Martin, of Louisville, I was supplied with crude "gum" collected in small amounts from single trees, and from the tests of these samples it appeared that the laevo-rotation was

found only in the product from the so-called spruce trees, sparingly represented in the lower turpentine-producing region. As this spruce pine (*P. glabra*) is not considered important from the standpoint of the industry I found difficulty in securing material enough for satisfactory investigation. However, in April of this year six samples of the dip, or crude liquid exudation, collected near Mobile, from as many different trees, were sent me and from these I distilled the oils used in the tests below.

In odor, color, specific gravity, and boiling-point these oils showed no unusual features, the average specific gravity at $\frac{20°}{4°}$ being 0.862. When examined by the polarimeter, using the 200 mm. tube, I found the "observed angle of rotation," α, as follows:

No. 1	$\alpha_D =$	$-64.750°$
" 2	"	$-69.075°$
" 3	"	$-64.541°$
" 4	"	$-63.100°$
" 5	"	$-63.333°$
" 6	"	$-70.333°$

The laevo-rotation is in all cases very marked, the specific rotation in the last amounting to

$$[\alpha]_D = \ldots\ldots\ldots -40.79°$$

It is also interesting to note that the results are close for the six samples, but as the trees yielding them grew in the same orchard, and, therefore, under practically the same conditions, and as the samples were taken at nearly the same time, this agreement should not be unexpected. It may be recalled that the laevo-rotation of the French oil has usually been found much more uniform than the rotation of the American oil.

These observations seem to show the probable correctness of my former suggestion; *viz.*, that the negative rotation sometimes found in American oil may be due to the presence of products from spruce trees. This appears all the more probable when it is remembered that in numerous oils examined, known to be free from spruce, a marked positive rotation was always noted, while a low positive rotation was found only in those oils distilled in parts of the country where the spruce is occasionally found.

In the further study of these oils I mixed distillates 1 and 3 above and redistilled fractionally. The fractions were polarized as before with the following results:

Temperature.			a_D in 200 mm. tube.
156.	to	156.7	−69.133°
156.7	"	157.2	−67.683°
157.2	"	157.6	−65.930°
157.6	"	159.4	−63.200°
159.4	"	162.7	−57.883°

A mixture of 2 and 6 gave:

Temperature.			a_D in 200 mm. tube.
156.	to	156.2	−73.350°
156.2	"	156.7	−72.416°
156.7	"	157.2	−71.066°
157.2	"	158.7	−68.865°
158.7	"	162.7	−65.160°

These results confirm those obtained from other oils, showing that the absolute amount of rotation is decreased in the higher fractions.

It was stated by Berthelot (J. B., *1853*, p. 522) that the dextro-rotatory American oil when heated in sealed tubes to above 250° is transformed into a substance with higher boiling-point and negative rotation. To test this behavior in the present case I heated a portion of the first fraction from 1 and 2 to a temperature of 280° during two hours in a sealed glass-tube. On cooling it was polarized without redistillation, and showed in the 200 mm. tube

$$a_D = \ldots\ldots\ldots\ -15.33°.$$

The product was then sealed and heated again to 300° through several hours. On cooling, it was found to be yellowish and somewhat viscid; on distillation the liquid was found to have a much higher boiling-point than the original turpentine, but little passing over below 170°.

Three-fourths of the product distilled between this point and 250°, and this portion polarized gave in the same tube

$$a_D = \ldots\ldots\ldots\ -19.560°.$$

A fraction of the distilled liquid collected from 175°–180° was strongly laevo-rotatory also.

The residue was very dark and became thick and resinous on

exposure to air. The distilled liquid had a marked odor of oil of lemons and this with its rotation suggest that it must be identical with the product described by Berthelot as iso-terebenthene, which may be obtained also from the laevo-rotatory French oil. While the ordinary product of long heating of turpentine-oil seems to be inactive dipentene we have here a very stable active product which is probably mainly laevo-limonene.

CHICAGO, October 22, 1894.

IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.

BY G. DE LAIRE AND FERD. TIEMANN.

[TRANSLATED AND ABRIDGED BY S. S. EMERY.]

(*Continued from Page 411 of Volume XV.*)

Iretol.—Iretol, the third decomposition product of irigenin, may be separated from the alkaline solution of the three by supersaturating with dilute sulphuric acid (1 : 2), neutralizing with potassium carbonate, and, after filtering from the separated potassium sulphate, shaking ten to twelve times with ether, which dissolves only the iretol. The ether can not be completely distilled from this extract, as the crude iretol forms condensation products which are insoluble in water and ether; hence the last portion of the ether must be allowed to evaporate in the air. The iretol thus obtained is a crystalline mass, easily soluble in water, alcohol, ether, and acetic ether. By fractional precipitation by chloroform from the acetic ether solution it is obtained as white needles, melting at 186°.

Its molecular weight was found to be:

1. By the lowering of the freezing-point of a glacial acetic acid solution. (Raoult's method.)	2. By the raising of the boiling-point of an alcoholic solution.	Calculated for $C_7H_8O_4$.
181.2	159	156

It contains one methoxyl group, as shown by the following determinations:

ANALYSIS.

	Per cent. (OCH_3).
Calculated for $C_6H_5O_3(OCH_3)$	19.87
Found	17.26—19.22

Tribenzoyliretol, $C_7H_5O_4(CO.C_6H_5)_3$. — Tribenzoyliretol is obtained by treating an absolute alcohol solution of one molecule of iretol and three molecules of sodium ethylate with a slight excess of benzoyl chloride and letting stand several days in the cold. It is separated by removing the alcohol by steam, extracting with ether, and, after shaking with dilute soda solution, evaporating, when it is obtained as an oily substance, which solidifies after several weeks to a transparent resin, easily soluble in alcohol, ether, acetic ether, benzene and chloroform, but insoluble in water and ligroin.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{28}H_{20}O_7$	71.79	4.27
Found	71.03	4.68

From the foregoing, it is evident that iretol contains one methoxyl and three hydroxyl groups, and that its empirical formula is $C_6H_2(OCH_3)(OH)_3$, according to which iretol appears to be the monomethyl ether of a tetroxybenzene. The correctness of this view is established by the conversion of iretol into phloroglucinol.

This is accomplished by treating the cold dilute (1 : 10) aqueous solution with sodium amalgam, and, after destroying the excess of amalgam by heating on the water-bath, adding a slight excess of sulphuric acid and then distilling. The distillate consists of very dilute methyl alcohol with traces of acetone. The ether extraction of the residue, on evaporating, gave pure phloroglucinol, melting at 208°, its identity being established by the following:

ANALYSIS.

	Per cent. water of crystallization.
Calculated for $C_6H_6O_3.2H_2O$	22.22
Found	22.38, 22.92

	Per cent. C.	Per cent. H.	
Calculated for $C_6H_6O_3$	56.98	4.76	In the anhydrous phloroglucinol.
Found	59.94, 56.71	4.64, 4.70	

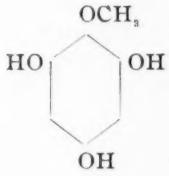
	Molecular weight.
Calculated	126
Found (raising of boiling-point of alcoholic solution)	121

The triacetyl derivative formed from the phloroglucinol melted at 106° (104°–106° according to Hlasiwetz[1] and Herzig[2]). Finally, we prepared tribenzoylphloroglucinol $C_6H_3(OCOC_6H_5)_3$, crystallizing from alcohol and melting at 172°.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{27}H_{18}O_6$	73.97	4.11
Found	73.40	4.10

The phloroglucinol is formed from the iretol according to the equation $C_7H_8O_4 + 2H = C_6H_6O_3 + CH_3OH$, from which it is evident that iretol is a methoxyphloroglucinol, having the constitutional formula



Properties and Reactions of Iretol.—Melts at 186°; easily soluble in water.

(*a*) *In Aqueous Solution.*—Violet color, changing to brownish red, with ferric chloride.

Red precipitate of benzeneazoiretol with anilin nitrate, sodium nitrite, and a few drops of strong acid.

(*b*) *In Alcoholic Solution.*—A white, crystalline condensation product with a solution of benzaldehyde in six times its volume of concentrated hydrochloric acid. Substitution of vanallin for benzaldehyde gives violet-colored solution before precipitation.

The last three tests are characteristic, although also given by resorcinol and phloroglucinol.

(*c*) *With Bromine.*—In ethereal solution, gives bromine substitution products.

In ethereal solution in the presence of water gives hexabromacetone, $Br_3C.CO.CBr_3$.

[1] *Liebig's Annalen*, 119, 201.

[2] *Wiener Monatshefte für Chemie*, 6, 888.

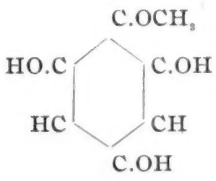
Bromine in caustic alkali, instead of free, gives bromoform, the hexabromacetone first formed being readily decomposed by the alkali into carbon dioxide and bromoform.

Sodium nitrite, with acetic acid in slight excess, converts it into the sodium salt of dinitrosoiretol, $C_7H_3NaN_2O_5.2H_2O$, separating in red crystals.

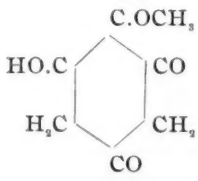
Tetroxybenzene 1.2.3.5.—The methyl in the methoxyl group of iretol can be easily replaced by hydrogen, by heating with dilute hydrochloric acid in a closed tube. Monochlormethane is given off. After removing the hydrochloric acid with lead and silver carbonate, and the water by evaporation in a partial vacuum, the tetroxybenzene was obtained as an amorphous substance, soluble in water, alcohol, ether, acetic ether, but insoluble in benzene, chloroform, and ligroin.

Isomerism of Iretol.—The properties and reactions of iretol, and also the difficulty in obtaining pure the corresponding tetroxybenzene, are explained by its isomerism, its two forms being

I.



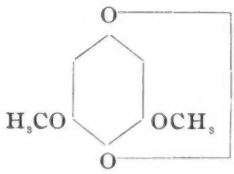
II.

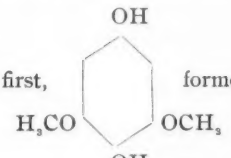


Form II undergoes hydrolysis on treating with alkali, acetone, and acetic acid being found.

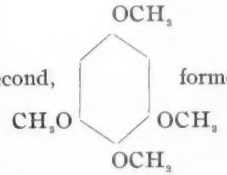
This isomerism is substantiated by the following:

Methyl Derivatives of Iretol.—Tetroxybenzene yields a di- and tetra-methyl ether, prepared from the dimethoxyquinol





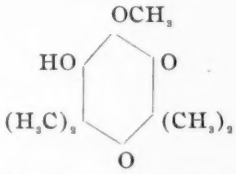
the first, formed by reduction of the quinol, and the



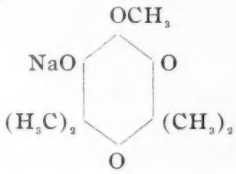
second, formed by methylating the dimethyl product.

We have not succeeded in preparing this last from iretol.

Tetramethyliretol



is prepared by treating the methyl alcohol solution of iretol (five grams) in an atmosphere of hydrogen, with sodium (three grams) dissolved in methyl alcohol, and with iodomethane (twenty grams). The methylation is induced by shaking the flask, and is accompanied by a rise of temperature. The sodium salt of tetramethyliretol is separated by evaporating and precipitating with concentrated caustic soda. The yield is about one-third of the theoretical, the remainder of the iretol being converted into oily methyl derivatives. The salt crystallizes in long white needles, with three molecules of water, and suffers efflorescence, at ordinary temperatures, in a partial vacuum. Its constitutional formula is



ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. Na.	Per cent. H_2O.	Per cent. OCH_3.
Calculated for $C_{11}H_{15}NaO_4.3H_2O$ (=$C_{11}H_{21}NaO_7$)	45.83	7.29	7.98	18.75	10.76
Found	45.57, 45.50	6.94, 6.99	7.76, 7.75	18.82, 18.20	10.74
In the anhydrous salt:					
Calculated for $C_{11}H_{15}NaO_4$	56.41	6.41	9.83		
Found	56.55, 56.04	7.17, 7.18	9.70		

Sulphuric acid liberates free tetramethyliretol, insoluble in ligroin, but soluble in hot water, alcohol, ether, acetic ether, benzene, and chloroform. It crystallizes in glistening white needles, with one molecule of water, melting at 97°; effloresces in a partial vacuum, the anhydrous substance melting at 104°.

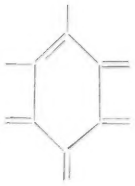
ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. H_2O.
Calculated for $C_{11}H_{16}O_4.H_2O$, (=$C_{11}H_{18}O_5$)	57.39	7.83	7.83
Found	56.98	7.86	8.06
In the anhydrous substance:			
Calculated for $C_{11}H_{16}O_4$	62.27	7.55	
Found	62.41	7.51	

Benzoyltetramethyliretol, $C_{11}H_{15}(COC_6H_5)O_4$, formed by the action of benzoylchloride on the sodium salt of tetramethyliretol in alcoholic solution, crystallizes therefrom in white tablets, melting at 84°.

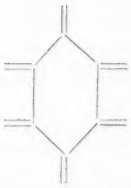
From the constitutional formula of tetramethyliretol (page 851), it is evident that by oxidation it breaks up into dimethylmalonic acid, isobutyric acid, and formic acid. By fusion with caustic potash, these products were actually obtained.

Dihydrotetramethyliretol.—Tetramethyliretol is a derivative of tetrahydrobenzene.



On treating with sodium amalgam, at ordinary temperature,

it takes up two atoms of hydrogen, apparently passing into the hexahydrobenzene form

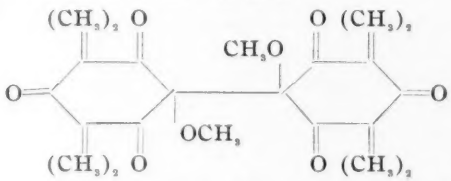


and this view is substantiated by the conversion of iretol into phloroglucinol. After destroying the excess of amalgam by heating on a water-bath, the sodium salt of dihydrotetramethyliretol may be crystallized out, or the free dihydrotetramethyliretol may be obtained by acidifying before crystallizing, when it forms transparent, rhombohedral crystals, containing one molecule of water, which is slowly given off on standing in a partial vacuum. The crystallized substance melts at 107°, the anhydrous at 139°. It is easily soluble in water, alcohol, ether and chloroform, and is precipitated from the latter by ligroin. It is not attacked by bromine nor permanganate, and, in general, does not differ widely from the tetramethyliretol.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{11}H_{18}O_4.H_2O$	56.90	8.62
Found	56.90	8.67
In the anhydrous substance:		
Calculated for $C_{11}H_{18}O_4$	61.68	8.41
Found	61.71	8.72

Dehydroditetramethyliretol, $C_{22}H_{30}O_6$.—



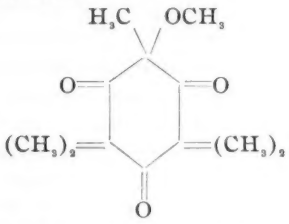
This is formed by the action of ferric chloride on the aqueous solution of sodium tetramethyliretol, two molecules, of which unite, each losing one atom of hydrogen. The precipitation

is attended with a change of color of the solution into deep violet, passing into olive-brown, and finally clear green. It forms white needles, melting at 133°, easily soluble in alcohol, ether, benzene, and chloroform, but insoluble in water. It is very stable, having, in general, the properties of a saturated compound.

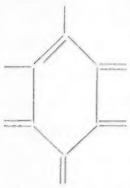
ANALYSIS.

	Per cent. C.	Per cent. H.	Molecular weight.
Calculated for $C_{22}H_{30}O_8$	62.64	7.11	422
Found	62.49	7.14	367

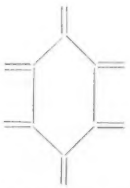
Pentamethyliretol, $C_{12}H_{18}O_4$.—



This is formed by further methylation of the sodium tetramethyliretol by means of methyl iodide. According to this, it is a derivative of tetrahydrobenzene,



and not of hexahydrobenzene.



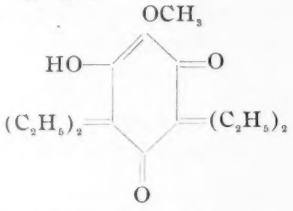
As it has, in general, the properties of a saturated compound, it was thought that rearrangement of the atoms in the molecule of the tetramethyliretol must have taken place in the above process, and this is proved by the methoxyl determination, which shows the presence of but one methoxyl group.

ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. OCH_3.	Molecular weight.
Calculated for $C_{11}H_5(OCH_3)O_3$	63.72	7.97	13.72	226
Found	63.62	7.98	13.63	190

It crystallizes from a methyl alcohol solution in long white needles, melting at 62°, boiling at 240°, and slowly subliming at ordinary temperatures.

Tetraethyliretol, $C_{16}H_{24}O_4$.—



This was prepared similarly to the corresponding methyl compound. That its constitutional formula is analogous to the latter is shown by the methoxyl determination in the following

ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. OCH_3.
Calculated for $C_{14}H_{21}(OCH_3)O_3$	67.16	8.95	11.57
Found	67.21	9.19	13.81

Its sodium salt being somewhat soluble in caustic soda, it is difficult to isolate from the other products of the reaction, but it may be accomplished by first removing them with ether, when it may be crystallized from the chloroform and acetic ether extraction of the residue by precipitating with ligroin. It forms white, anhydrous prisms, melting at 168°–169°.

Analogous to the trimethylether of phloroglucinol,

$$C_6H_3(OCH_3.1.3.5)_3$$

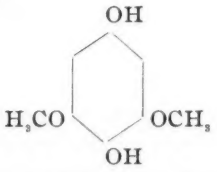
(prepared by saturating the methyl alcohol solution of phloroglucinol with hydrochloric acid gas, and then further methylating the dimethyl product thus formed by using methyl iodide in alkaline solution), we have attempted to prepare the trimethylether of iretol, the tetramethylether of asymmetrical tetroxybenzene, but as yet, without success.

Monomethyliretol, $C_6H_2(OCH_3)_2(OH)_2$.—This is the dimethylether of asymmetrical tetroxybenzene. It is formed by the action of hydrochloric acid gas on the methyl alcohol solution of iretol at 0°. When freshly prepared it is of oily appearance but slowly solidifies to a crystalline mass. When crystallized from boiling benzene it forms white tablets, melting at 87°, easily soluble in

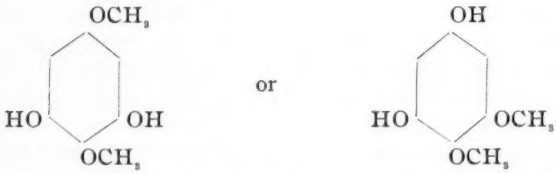
water, alcohol, and ether, but less soluble in benzene and chloroform.

It may be further methylated by the action of methyl iodide on its sodium salt, but instead of obtaining thus a normal asymmetrical tetroxybenzene ether, polymethyl derivatives of methyliretol result, since the methylation takes place in the benzene ring.

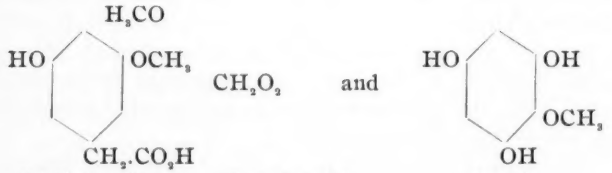
The dimethylether,



prepared from the unsymmetrical tetroxybenzene differs completely from the monomethyl iretol. Hence, the latter conforms to one of the two formulas:



Constitution of Irigenin and Iridin.—Irigenin has the formula $C_{18}H_{16}O_8$. By hydrolysis it takes up three molecules of water and breaks up into



Iridinic acid. Formic acid. Iretol.

Iridin, also, can undergo hydrolysis.

The presence of two phenol groups in irigenin is demonstrated by the formation of the dibenzoylirigenin and the diacetylirigenin; the unstability of diacetyl derivative relative to the

monoacetyl derivative, indicates that these phenol groups are not similarly situated in the irigenin molecule.

We have not yet been able to crystallize the hydrolyzed irigenin, but, by converting it into its potassium or sodium salt (accomplished by treating its absolute alcohol solution with sodium or potassium ethylate) we have thus been able to effect its isolation. From the analysis of these salts is made clear the reaction of the hydrolysis.

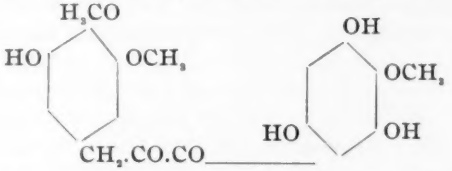
ANALYSIS.

($C_{24}H_{25}K_3O_{14}$ and $C_{24}H_{25}Na_3O_{14}$.)

	Per cent. K.	Per cent. Na.
Calculated	17.96	11.39
Found	18.32	11.69

If, now, instead of using an *excess* of potassium ethylate, only the amount sufficient to form the tribasic salt be taken, a *di*-basic salt is always the result, which indicates that one of the hydroxyl groups of the hydrolyzed irigenin is of a weaker acid character than the other two. Consequently, the first product in the hydrolysis of iridin is $C_{18}H_{14}O_5(OH)_3(OC_6H_{11}O_5)$, and, for irigenin, is $C_{18}H_{14}O_5(OH)_4$.

Since the hydrolyzed irigenin is a relatively sable compound, not being attacked by reagents which effect the saponification of ether, we conclude that the two portions of the irigenin molecule, representing respectively iridinic acid and iretol, are not linked together by an oxygen atom, but are held together by a chain of carbon atoms, as shown in the following formula:



According to this formula, the hydrolyzed irigenin is an α di-ketone. This is further proved by the similarity of its reactions with alkali reagents and those of benzene, the latter, in the presence of potassium cyanide, yielding benzaldehyde, and benzoic acid, while the former yields iridinic acid, or aldehyde, and a carboxyl derivative of iretol.

This is more particularly shown by the formation of the same aldehyde by the decomposition of irigenin, and also synthetically from iretol. In the first case, the hydrolysis of the irigenin was effected by dilute caustic soda. After precipitating with sulphuric acid and filtering, soda solution and potassium cyanide were added to the solution. After standing some eight days, it was acidified and extracted with ether. The aldehyde was separated from the ether extract by sodium bisulphite. By cautiously decomposing with sulphuric acid, and shaking with ether, the aldehyde was obtained as a syrup, which, on digesting six hours with alkali, gave the theoretical amount of formic acid.

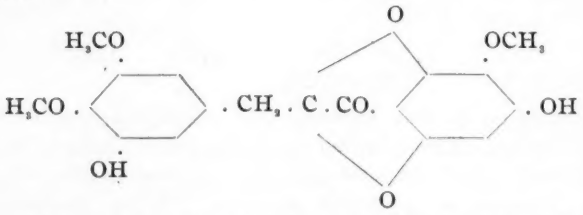
The synthesis of the aldehyde from iretol was effected by the action of chloroform and caustic soda on iretol in an atmosphere of hydrogen. After removing the chloroform by evaporation, the aldehyde was separated as above, it was also, in like manner decomposed, yielding iretol and formic acid.

The hydrolyzed irigenin, by taking up the elements of water, breaks up into iridinic acid and iretol aldehyde, this latter subsequently being converted into iretol and formic acid. Analogous to this is the decomposition of phloroglucinolcarboxylic acid into phloroglucinol and carbon dioxide, by boiling its aqueous solution.

From the foregoing, we feel justified in giving irigenin the formula

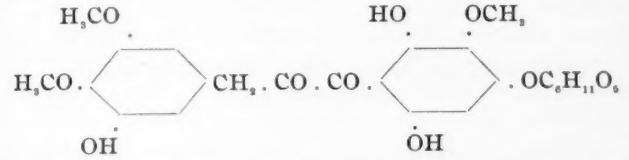
$$(H_3CO)_2(HO)C_6H_2.CH_2.CO.CO.C_6H_2(OCH_3)(OH)_2.$$

The irigenin itself contains one less molecule of water, and, in accord with all the reactions described, has the following constitution:

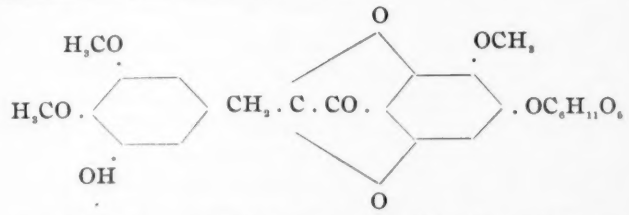


The iridin contains the glucoside residue, $OC_6H_{11}O_5$, in place of one of the two hydroxyls of irigenin.

We have previously noted the weaker acid character of one of the three hydroxyls of hydrolyzed iridin relative to the other two; we have also remarked that in titrating iridinic acid, $(H_3CO)_2.C_6H_2(OH)(CO_2H)$, with caustic soda and litmus, the end-point is obtained as soon as the hydrogen of the carboxyl group has been replaced by the alkali. From these two considerations we conclude that in the hydrolyzed iridin, the hydroxyl having the weakest acid character is found in the iridinic acid nucleus. Consequently, the constitution of hydrolyzed iridin is



Finally, if the above results and conclusions are correct, iridin itself has the constitutional formula



In closing, we would add a word regarding the probable relation of iridin and irigenin to the sugars; both are carbohydrates, and, as without doubt, the sugars are the first products changes of the plant matter, it appears probable that iridin and irigenin are formed from three and four molecules of sugar respectively, by the splitting off of eleven and ten molecules of water. In reviewing the possible methods of the formation of sugars from benzene derivatives, our attention is called to "cyclo" sugars, formed by an aldol condensation between the first and sixth groups of the chain in hexanpentolal

$$\overset{1}{HOC}.\overset{2}{CHOH}.\overset{3}{CHOH}.\overset{4}{CHOH}.\overset{5}{CHOH}.\overset{6}{CH_2OH}.$$

This, perhaps, is the manner in which inosite is formed. Since the pinite occurring in some resins has been proven by L. Maquenne[1] to be the monomethyl ether of an inosite, and, as the latter, by the symmetrical splitting off of three molecules of water, yields phloroglucinol, and the former, by losing two molecules of water, yields dihydroiretol, which can be converted into iretol by the removal of two atoms of hydrogen, the general relation of iridin to the sugars is better understood.

Our thanks are due to Dr. Paul Krüger, and to Dr. Richard Schmidt, for their valuable assistance in prosecuting this investigation.

BOTRYTIS BASSIANA AND ITS CRYSTALLINE PRODUCTS.[2]

By E. Verson.

AMONG the alterations produced by *botrytis bassiana* almost all authors note an abundant crystalline efflorescence which very often covers the small mummified bodies of the muscardin worms.

M. Dandolo in note 21 of his book, "*l' Art d' elever le verf à soie*," 1814, has written on this subject as follows: "As soon as I had observed attentively the worms or muscardin chrysalides I affirmed without hesitation that all this must be the consequence of chemical attractions and combinations."

It was in fact difficult to be mistaken after having seen the animal tissue altered in this manner and converted into a substance more or less hard and unalterable while before it was an animal substance easily decomposed. I put away with care the white saline substance which enveloped the so-called muscardin worms and afterwards analyzed it. Not being satisfied with my work I asked my learned friend, M. Brugnatelli, professor of chemistry at Pavia, to make an analysis of the material.

"The muscardin which covers the mummy of the worm or the chrysalide in the cocoon is composed principally of magnesium ammonium phosphate."

A like opinion was given by M. Lomeni (*Variétés agraires*

[1] *Ann. chim. phys.*, [6], **22**, 264.

[2] Read before the World's Congress of Chemists, Thursday, August 24, 1893.

économiques et technologiques, **3**, *1835*), who says: "The chemical analysis of this substance has proved to M. Dandolo and to the late Professor Brugnatelli that the efflorescence of the muscardin is a combination of magnesia, phosphoric acid, and ammonia. Professor Balsamo thinks also that the whitish efflorescence by which the worms are enclosed is entirely inorganic."

Mr. Charles Vittadini in his celebrated work, *Della natura del calcino o mal del segno* (*Journal de l' T. R. Instituto Lombardo di Sc. L. A.*, **3**), expresses an entirely different opinion on this subject.

"The cadavers of the muscardin worms," he says, "after being deprived of their efflorescence and kept in a humid state become covered, after several days, with a second efflorescence which has also the appearance of a muscardin; but this is formed by myriads of fine crystals produced by the final chemical metamorphosis of the cadaver. These crystals observed by the naked eye have the form of diverging bunches of needles like a brush or of rounded masses which resemble the sea-urchin. They are transparent, colorless, or slightly reddish. The crystals dissolved in warm water show a decidedly acid reaction which becomes more sensible by evaporating the solution; on being treated with caustic potash it gives off a strong ammoniacal odor; the geometrical figure consists of long prisms with a rectangular base with cuneiform extremities."

"The reaction obtained by M. Cardoné on a small quantity of the crystals indicates a combination of alloxanic acid and ammonia with small quantities of potassium and calcium. In fact during the new process of crystallization a thick reddish liquid, generally alkaline, of a strong ammoniacal odor, flows off the cadaver of the worm and deposits a considerable quantity of crystals."

This secondary efflorescence, which takes place not only on the surface of the cadaver but extends to all the interior tissues by giving them an almost vitreous appearance, explains to a certain extent the doubt expressed by some observers that the *botrytis* is nothing else than simple crystallization.

I cite only these three authors who agree with what the literature furnishes on the nature and composition of the efflorescence

and do not mention others who have investigated the crystalline efflorescence and its different properties.

The worms mummified by the muscardin, consist always of a plentiful crystalline substance which, dispersed between all the tissues, is accumulated in considerable quantities in the inside of different parts of the somatic cavity. But it is to be remarked that the crystals do not always have the same exterior appearance; this depends on the humidity of the surrounding atmosphere. When kept perfectly dry from the beginning the crystalline substance remains inside of the cutaneous integument and consists of very fine needles which impregnate all the tissues. In an atmosphere more or less humid the cadaver when it begins to dry, exudes on the surface a dense reddish humor, which forms a crust of an earthy appearance. The microscope shows that the exuded substance notwithstanding its amorphous appearance is mostly of a crystalline nature and is not different from the substance left and dispersed between the interior viscera.

Finally, if we place the fresh cadaver in a warm place, more or less closed and saturated with moisture we will see after a certain time the crystallization in the sea-urchin forms which rupture the superficial integument. Often they are disposed without order in different parts of the body but generally are to be found in both extremities and where the visceral volume does not hinder a larger expansion of the somatic cavity.

It is to be remarked that the formation of the sea-urchin crystallizations is not limited to the time immediately following the death of the worm. I was able to obtain it from cadavers mummified some months before by placing and keeping the cadavers during some weeks in a humid warm place. By means of two needles these crystals can be removed from the cadaver like the stone from a dried fruit.

By this method I was able to provide myself with a certain quantity of material though not free from mechanical impurities and of reddish appearance. By dissolving it in warm water, filtering, and concentrating the filtrate at a moderate temperature I obtained a crystalline mass which on being redissolved, recrystallized two or three times, and separated from the mother-liquor, were obtained perfectly pure. I may remark here that

although the warm water is of a moderate temperature (50°-60° C.) the solution of the crystals is always accompanied by the formation of very small bubbles which are probably carbon dioxide; in repeating this operation an insoluble residue always perceptible though very light is noticed. This is the reason which led us to believe that the crystals are not stable and liable to decompose even by dissolving in distilled water. That belief is fortified by the fact that I was never able to obtain the crystals in the sea-urchin form though under the microscope the crust of the second and third crystallization seemed to be composed of ordinary prisms with dihedral extremities.

The crystals of the sea-urchin form are easily soluble in distilled water and react decidedly acid. Dried and heated in a small test-tube which is covered by a piece of paper moistened with litmus solution they produce the following phenomena: without any visible change of appearance, they expel ammoniacal vapors which turn the litmus blue; by further heating they melt to an ash-colored, foamy mass, the bubbles expelling whitish vapors. On the neck of the tube small drops of a condensed liquid can be seen; in the upper part of the test-tube a ring of crystalline needles sublimes; the odor is strong and excites a cough; on the bottom remains a whitish compact residue with little carbon.

The solution obtained from the crystals does not show any change with hydrochloric and sulphuric acids; ammonium chloride, ammonia, and sodium phosphate form an abundant precipitate. Ammonium carbonate and caustic ammonia do not produce any visible reaction.

The solution remains clear on concentrating with platinum chloride or even with potassium antimoniate; calcium hydroxide sets free an abundant quantity of ammoniacal vapors. The residue left from evaporation on the salt-bath dissolved in nitric acid produces some insoluble flocks; the result is almost absolutely negative with molybdic acid.

Another portion of the liquid was treated with barium chloride and gave an abundant precipitate, soluble in hydrochloric acid; a white precipitate is obtained by treating with silver nitrate; calcium chloride gave a white precipitate on being added to the

alkaline solution; ferric chloride precipitates voluminous reddish flocks.

A portion of the solution of crystals obtained was precipitated with lead acetate; the precipitate was decomposed by hydrogen sulphide; the filtered solution after evaporating, left on the bottom rhombic prisms which, on redissolving, produced a white precipitate with calcium chloride insoluble in acetic acid. Heated in a small tube they sublime without residue, while heated with strong sulphuric acid they effervesce and evolve carbon dioxide and carbon monoxide.

Finally I investigated the residue of the calcined crystals of the sea-urchin form. This, when dissolved in hydrochloric acid, does not give any appreciable precipitate unless by adding ammonia, ammonium chloride, and sodium phosphate. After all the reactions I have mentioned above there can not be any doubt about the composition of the crystals. Not taking into consideration the impurities which can not be entirely removed and remain as undeterminable traces of potassium, phosphoric, silicic, and succinic acid, the crystals are composed mostly of *oxalic acid, ammonium, and magnesium.*

I have also determined the percentage composition of the crystals as completely as the small amount of material permitted.

I. Purified crystals, 0.0784 gram; dried at 100° C., 0.0686 gram; difference =0.0098; equal to 12.47 per cent. Dissolving the crystals in distilled water and treating the acidified solution with calcium acetate I obtained by the regular method 0.054 gram calcium carbonate which corresponds to 0.0389 gram oxalic acid or 49.62 per cent.

II. Purified crystals, 0.2572 gram; dried at 100° C., gave 0.2243 gram; difference 0.0329, equal to 12.80 per cent. Dissolved in distilled water and treated with calcium acetate gave 0.1727 gram calcium carbonate which corresponds to 0.1243 gram oxalic acid or 48.33 per cent.

III. Purified crystals, 0.1571 gram; dried at 100° C., 0.1376 gram; treated with milk of lime (Schloesing's method). After forty-eight hours the ten cc. of normal sulphuric acid was neutralized by only 8.06 cc. of normal caustic soda or 1.94 cc. of

normal sulphuric acid was neutralized by the ammonium of the crystals, which corresponds to 22.23 per cent.

IV. Purified crystals, 0.2560 gram; dried at 100° C., left 0.2243 gram; Schloesing's method for determination of ammonium gave 0.0576 gram of ammonium, equal to 22.50 per cent.

V. Purified crystals, 0.0789 gram; dried at 100° C., left 0.0690 gram. The hydrochloric acid solution precipitated with ammonium chloride, ammonia, and sodium phosphate, gave 0.0066 magnesium pyrophosphate, equal to 0.0015 magnesium or 1.9 per cent.

After the above determinations I conclude that the sea-urchin crystals of the muscardin after being purified by repeated crystallization, contain on an average:

	Per cent.
Water	12.635
Oxalic acid	48.975
Ammonium	22.365
Magnesium	1.900
	85.875

I regret that the amount of material was not sufficient for further investigations in order to find the fourteen per cent. necessary to complete the analysis. We could then establish whether the crystals contain any water which is separated at higher temperature than 100° C. We could also determine the carbon dioxide given off while dissolving the crystals in water and ascertain from comparative analysis the products of different successive crystallizations.

Nevertheless I believe the data we possess are sufficient cause to accept in full certainty that the crystals represent a double salt of oxalate of magnesium and ammonium.

I find described in the literature five double oxalates of the following formula of constitution:[1]

1. $C_2O_4Mg,7C_2O_4(NH_4)_2+8H_2O$.
2. $3(C_2O_4Mg),C_2O_4(NH_4)_2+2H_2O$.
3. $C_2O_4Mg,6C_2O_4(NH_4)_2+9H_2O$.
4. $5(C_2O_4Mg),13C_2O_4(NH_4)_2+H_2O$.
5. $C_2O_4Mg,5C_2O_4(NH_4)_2+10H_2O$.

of which the percentage compositions are as follows:

[1] Souchay et Lenssen, Kayser in *Poggend. Ann.*, 60.

For the first formula:—

	Per cent.
Oxalic acid	63.30
Magnesium	1.08
Ammonium	22.66
Water	12.95
	99.99

	For the Second, Per cent.	Third, Per cent.	Fourth, Per cent.	Fifth, Per cent.
Oxalic acid	76.52	61.23	62.26	58.66
Magnesium	7.82	1.19	2.36	1.33
Ammonium	7.82	21.47	18.40	20.00
Water	7.82	16.10	16.98	20.00
	99.98	99.99	100.00	99.99

Comparing the results obtained from our analysis with these figures we have to exclude without hesitation formulas 2 and 4 in which there is a considerably larger amount of magnesium than we have found. Taking into consideration the fact mentioned on the first pages of this investigation, that the crystalline spheres radiated from the muscardin worms are partly decomposed by dissolving in distilled water and the phenomena by which this decomposition is accompanied I believe there is no doubt that the essential cause of the change must be in the oxalic acid.

But as oxalic acid is rapidly diminishing the amount of ammonium and magnesium must increase in the products of each renewed crystallization.

This consideration compels me to lay aside also formulas 1 and 3 and prefer formula 5 as more nearly approaching the results obtained than any of the others.

I have already emphasized at the beginning of this work that the crystals of the sea-urchin form whose nature I have established, are only formed under certain circumstances. But if we enclose the cadaver in a warm and humid place we can on the contrary determine their development at our will.

It seems to me that this fact authorizes us to make a very interesting conjecture; namely, that the immediate action of the *botrytis* is limited to the production of oxalic acid. This remains principally free, being combined generally with very small quantities of lime and magnesia.

But if the surrounding circumstances produce the putrefaction of the cadaver and the development of ammonia, ammonium

oxalate is formed at the same time, which dissolves a certain amount of magnesium oxalate forming the double oxalate; only it then forms that peculiar crystallization to which we wished to confine our attention.

It is very remarkable that *botrytis bassiana* cultivated on nutritive gelatine produces oxalic acid in large quantities which I have separated in a crystalline form.

CLOSING ADDRESS DELIVERED BEFORE THE WORLD'S CONGRESS OF CHEMISTS, AUGUST 26, 1893.

By Albert B. Prescott.

IN this closing hour of the Congress the chair would congratulate its members upon the great interest and value of its transactions. In the wide attendance of European and American chemists, in the weight of the papers in the several divisions of chemical science, in the constant and increasing attendance through the sessions of six crowded days, and in the hearty spirit of brotherly sympathy which has given life and happiness to all our labors, we have been favored beyond the most sanguine expectations. We in the United States know the chemists of Europe better than we did before this Congress. Surely we have the best of encouragement for the union of the chemists of the world in a series of great meetings of profit and acquaintance, the first one of which is now being concluded.

I know that I voice the sentiment of every member when I give our united thanks to those whose active and untiring exertions have carried so well all the arrangements of this meeting. Our thanks are due, first, to the American Chemical Society, who instituted the call for the Congress and now opens its journal to our proceedings. To our general chairman of the joint committee, Professor Wiley, of the United States Department of Agriculture, we have been indebted for most efficient attention in details. He took the position when it was not easy to find one to accept its labors and to face its uncertainties. The chairman of the committee on papers, Professor William McMurtrie, and assuredly the chairman of the committee from the Congress Auxiliary, Professor John H. Long, the local

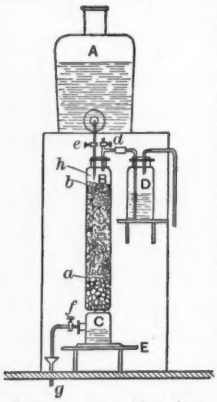
genius of our convention, will be remembered most gratefully by us all. I will not longer detain you from your personal farewells to each other, and now declare the Congress adjourned.

HYDROGEN SULPHIDE GENERATOR.

By H. G. Schanche.

Received September 13, 1894.

THE form of generator shown in the annexed cut has proved itself, during seven years of use, to always furnish an *absolutely uniform supply of gas.* The acid reservoir A delivers the acid into the generator B, containing ferrous sulphide, *a b*, resting on coarse pebbles at *a*. The ferrous chloride collects in C and may be drawn off, from time to time, by opening cocks *d* and *f*, thus allowing it to flow through the lead pipe *g* into a drip-pan underneath the table; D is an ordinary bottle for washing the gas. By regulating the flow of acid by means of the cock *e*, any supply of gas may be obtained, while the height of the column of ferrous sulphide, through which the acid percolates, assures an absolutely uniform supply of gas, as well as a complete neutralization of the acid. The shelf E, on which the generator B rests, can be slipped off its bracket, thus facilitating the removal of B for cleaning or charging.



[Contributions from the Chemical Laboratory, U. S. Department of Agriculture, sent by H. W. Wiley, No. 11.]

MODIFICATION OF KNORR'S EXTRACTION APPARATUS.

By Oma Carr.

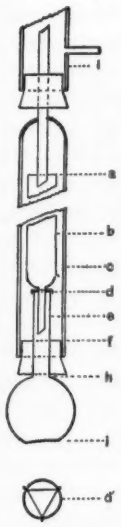
Received October 15, 1894.

TO avoid the inconveniences found with the usual form of mercury seal extractors,[1] such as the expense of flasks, disturbance of the seal by unequal pressures, tendency of the mercury to enter the flask, etc., the modification shown in the drawing is suggested.

The tube a b may be of any convenient size adapted to the

[1] Bulletin, No. 28, Division of Chemistry, p. 97.

inverted percolator-dome c. The top of the flask neck may be simply rounded in the flame, and the small triangle d d′ arranged to support the shoulder of the tube a b. The length of the flask between points d and h may be any desired distance, but it is suggested that it protrude above the cork f two inches. The cork f requires no previous extraction, as the solvent in contact with it can not enter the flask containing the extract except by volatilization. The flask may be of any desired size, although the ordinary "sugar flask," of 100 cc. capacity, without rim at the mouth, will be found convenient for the greater range of work.



Where it is desired to complete extract solutions to a definite volume the arrangement will be found particularly useful. The apparatus should be sunk in a water-bath to a depth sufficient to prevent accumulation of the solvent upon the cork f. The apparatus is simple and readily adapted to the condenser of the Knorr extractor, shown at l.

Upon completion of the extraction, the cork f is easily removed and the flask wiped and dried without danger or annoyance caused by mercury globules.

LABORATORY DEVICES.

By Elwyn Waller, Ph.D.

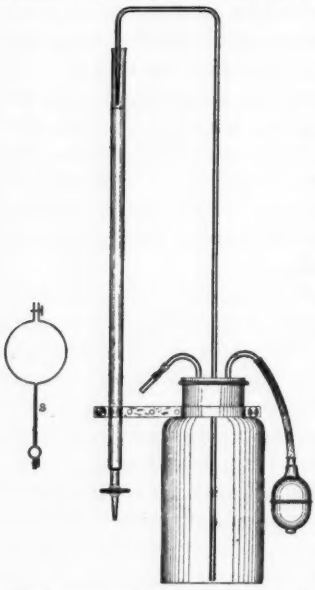
Received October 17, 1894.

DURING the recent general meeting of the Society in Brooklyn, many of the members visited the mineral water establishment of Dr. C. H. Schultz, in New York, and enjoyed his hospitality. After the lunch, the different parts of the plant were inspected by the visitors. In the analytical laboratory were a few forms of apparatus which attracted much attention as they have heretofore not been described. These were the burette-filling device, designed by Dr. A. P. Hallock, the chemist of the factory, the condenser and revolving Nessler rack, adapted by E. W. Martin, of the New York Health Department, and the Nessler comparator as improved by Dr. Hallock.

A description of these may be of service.

BURETTE FILLER.

Around the neck of a bottle of convenient size for the stock solution (capacity two liters or more) is fixed a collar of brass, carrying a clamp for the burette. The collar and clamp are made of two strips of brass bent as shown in the sketch, which are soldered or riveted together at s. The ends are turned outward, and fitted with thumb-screws, to allow the circles to be clamped firmly about the bottle neck and the burette.



The (rubber) cork of the bottle is pierced with three holes. Through one of these passes a tube extending from near the bottom of the bottle to above the top of the burette, then, turning twice at right angles it dips into the burette, being steadied in position there by a cork with a small slit on one side, or fitting loosely. The end of this tube is a little constricted, and cut off at a point corresponding with the zero line of the burette graduation.

Through another hole in the cork passes a short tube connected with an ordinary syringe compression bulb, by means of which air can be forced into the top of the bottle.

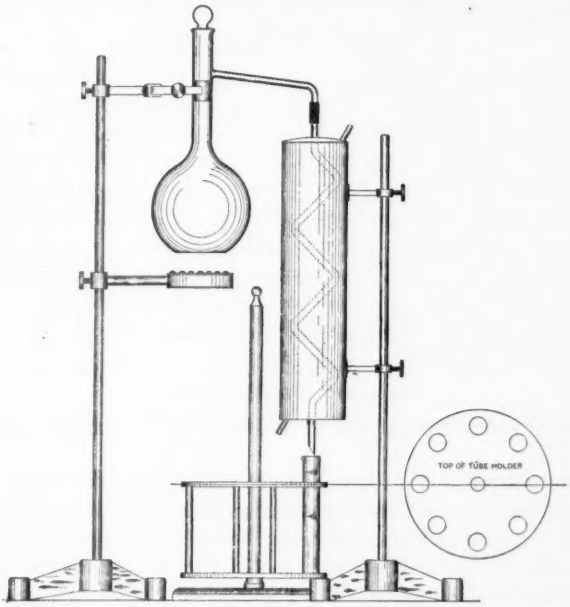
Through the third hole passes another short glass tube, the external end preferably bent downward, so that it may be easily closed by the finger when it may be desired to compress the air in the bottle, or by taking the finger away, the pressure may be at once released.

When it is desired to fill the burette, by closing the air-tube with the finger, and squeezing the bulb a few times, the stock solution is forced over into the burette. As soon as the level of the liquid has come to or above the zero line, the air pressure is released by removing the finger, and all the liquid above the

zero mark siphons back into the stock bottle, leaving the burette filled to the zero mark and ready for use.

The device is simple and comparatively inexpensive, and it has the great advantage that the delivery ("nose") of the burette can be easily fixed at a convenient height above the working table.

Serious objections to most other forms of apparatus constructed for this purpose are, that the delivery of the burette is too high above the working table, or that the stock-bottle has to be fixed



in some elevated position, or that the form of burette which must be used is an elaborate and costly piece of glass-blowing.

CONDENSER.

For water analysis distillations, etc., a glass-stoppered flask with side-neck tube is used. The end of the side-neck tube is turned vertically downward, being thrust deeply into the tin tube of the condenser, and held in place there by a short piece

of rubber tubing. The three-eighths inch block tin pipe forming the condenser-tube is bent zigzag instead of in the conventional helix. This affords a more even flow of the distillate. The cylindrical copper jacket containing the water for cooling is about four inches in diameter, and fifteen inches long. The disk closing the lower end is *arched upward* so that in case the condenser "sweats" from the use of very cold water, the drip from the outside can not contaminate the distillate. The lower end of the tin tube is cut aslant for the more certain delivery of the distillate.

REVOLVING NESSLER STAND.

This is simply a whirligig rack made of two circles of thin board connected with light strips of wood, the upper circle perforated to carry eight or ten tubes, the lower partly perforated to form shallow sockets for the tubes. The rack revolves about an upright set in a base. With such a stand as this, if one tube in the rack is placed in position to receive the drip from the condenser, revolving the rack will bring successively every other tube on the stand into the same position. The danger of upsetting or breaking the tubes is practically eliminated, and, moreover, the order in which the fractions of the distillate are taken off is easily preserved.

NESSLER COMPARATOR.

This has the form of a large test-tube rack of wood, painted black.

At the bottom is placed a strip of milk glass, extending from end to end, held in place by small pieces of rubber (ends of a small rubber cork) fastened to each side by small screws. The edges of the rubber are put so close to the bottom board that the glass can be just forced in between, and when in place it is firmly held.

About two inches above this is a strip of clear glass resting on cleats at the sides of the rack, fixed in place in the same manner as above described, and upon this clear glass the Nessler tubes stand. The necessity for raising the tubes from the white background, in order to make a comparison is thus obviated, and the whole apparatus may be very readily cleaned and kept in

condition. The drawbacks in the use of white paper for a background which may be easily wetted or stained are removed.

It has been found convenient to use a rack of ten or twelve holes, since with that the standards can be placed in every other hole, leaving the vacant spaces for the tubes to be compared.

NEW BOOKS.

LESSONS IN QUALITATIVE AND VOLUMETRIC CHEMICAL ANALYSIS FOR THE USE OF PHYSICIANS, PHARMACISTS, AND STUDENTS. BY DR. CHAS. O. CURTMAN; INCLUDING LESSONS IN QUALITATIVE CHEMICAL ANALYSIS, BY DR. F. BEILSTEIN. Fourth edition. St. Louis, Mo.: John L. Boland Book and Stationery Company. 1894. Price $1.50.

This new edition of a work intended primarily for students of medicine and pharmacy, contains chapters on manipulations of chemical apparatus, qualitative analysis (inorganic), examples for practice in the analysis of organic substances (proximate), volumetric analysis, examination of drinking water, and urine analysis. The author says the section on volumetric analysis "contains numerous examples illustrating every important volumetric method and forms a complete commentary on the volumetric assays of the new U. S. Pharmacopeia." The book contains a number of cuts illustrating various forms of apparatus, urinary sediments, several pathologic micro-organisms, and two charts of spectra. Meyer and Seubert's atomic weights are used. "The orthography has been adapted to the rules of the Chemical Section of the A. A. A. S."

To cover so large a part of the domain of analytical chemistry within a space of 300 octavo pages has required the constant and severe abridgment of methods allowing no opportunity for a discussion of their merits. The author has accomplished his purpose with more than ordinary success. As a rule he has shown excellent discrimination in the choice of methods, and has in some cases introduced matter one would hardly expect to find in so small a work, *e. g.*, Gutzeit's, Fleitmann's, and Bettendorf's tests for arsenic. Physicians and pharmacists will doubtless find the work a useful one. In some cases brevity of treatment has led to dogmatic statements that are liable to be wrongly interpreted by those having little knowledge of the subject under

discussion. Examples of this kind may be found in the chapter on the examination of drinking water. One having had experience in the matter would hardly be willing to state that "albuminoid ammonia may be considered as *proof of sewage actually present*, etc.," p. 244,—the italics are the authors. Other examples of a similar kind might be quoted. Standards of organic impurity in drinking water—a dangerous subject even for experts—can not be arbitrarily established, and the wise analyst will express a positive opinion only as he knows the history of the sample of water under examination. W. W. DANIELLS.

LABORATORY MANUAL OF ELEMENTARY CHEMICAL PHYSIOLOGY AND URINE ANALYSIS. BY JOHN H. LONG, M.D., Sc.D., PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES IN THE SCHOOL OF MEDICINE AND PHARMACY OF NORTHWESTERN UNIVERSITY. Small 8 vo., pp. 360 and index. Chicago: E. H. Colegrove & Co. Price, $2.50.

This work is a decided departure from the methods of the laboratory text-books usually offered to medical students. It joins the exercises in physiologic chemistry with those of applied medical chemistry, a plan that will increase the interest and value of the course. All through the book we find evidence that it is written from practical experience and is an evolution of years of teaching.

In the preface Dr. Long discusses briefly the unsatisfactory state of teaching at medical schools. He expresses the feeling growing among those engaged in teaching chemistry at such schools, that the general principles of the science should be made an entrance requirement.

The first part of the book, one hundred and seventy pages, comprises the chemical physiology. Methods of investigation are presented in considerable detail. Especially noticeable is the essay on polarimetry. Reference occurs as frequently in organic chemistry and physiology to rotation of the polarized ray, and the phenomenon is now recognized as having so direct a relation to molecular structure, that it is wise to give it full explanation. Numerous illustrations of the form and action of polarizing apparatus are given.

Part II, on Urine Analysis, comprises over one hundred and

sixty pages, and includes all that is required for the medical course.

We must express a regret that the spelling is old-fashioned. A teacher in a medical school may be excused from going to the full length of using "sulfate," "sulfid," etc., since the new pharmacopeia has refused to adopt these forms, but the useless final "e" might be dropped in many cases, and general usage permits the abandonment of the diphthong "æ" in all English words. We should prefer, therefore, "hemin" to "hæmin." It is pleasing to note that the approved term "glycerol" is used.

Several useful tables are included in appendix.

There are numerous illustrations of apparatus and of microscopic appearances of important structures. The work will be of great service in the field to which it is devoted. H. L.

THE CHEMISTRY OF PAPER-MAKING. TOGETHER WITH THE PRINCIPLES OF GENERAL CHEMISTRY. A HANDBOOK FOR THE STUDENT AND MANUFACTURER. BY R. B. GRIFFIN AND A. D. LITTLE. 8 vo. pp. 517, 99 illustrations. New York: Howard Lockwood & Co. 1894. Price, $5.00.

The scope of this book is sufficiently indicated in the title. One hundred of the opening pages are devoted to elementary chemistry, evidently intended for the manufacturer who knows little chemistry or has forgotten it; perhaps this was necessary; for chemists who buy the book it is certainly superfluous. Regarding the remaining pages it may be said that the authors display practical as well as theoretical knowledge of the subject, and the result is an entirely satisfactory treatment. They seem to be investigators as well and have embodied in nearly every section some valuable matter derived from their own experience. This will is especially true of those sections of the book treating of the chemical analysis and of paper-testing, which, to most chemists, prove its most valuable features. The treatment of these sections is thoroughly common sense and shows both knowledge and good judgment. Fourteen pages are given to an account of cellulose and its derivatives and their properties; then we have thirty-four pages on the various fibers. Following this, seven pages are devoted to an account of the processes for isolating cellulose. Seventeen pages are given to the soda process,

one page to the sulphate process, and nearly 200 pages to the sulphite process. Next comes Bleaching, twenty-six pages; Sizing and Loading, nineteen pages; Coloring, nine pages; Water, nineteen pages; Chemical Analysis, seventy-two pages; Paper-Testing, thirty-two pages; Electrolytic processes, eleven pages, and an appendix and index. Among other things, the appendix contains an account of the interesting thiocarbonates of cellulose discovered by Cross and Bevan, and a list of United States patents relating to the sulphite process. In brief, the book is an excellent one: well written, well printed, and well illustrated, and worthy of a place on the book-shelf of the chemist.

E. H.

A SHORT HISTORY OF CHEMISTRY. By F. P. VENABLE, PH.D. 12 mo. pp. viii; 163. Boston: D. C. Heath & Co. 1894. Price, $1.00.

The author, who is Professor of Chemistry in the University of North Carolina, has, for several years, given lectures to his students on the history of chemistry, and this little volume is an outgrowth of those lectures. The subject is divided into six Parts: I. the Genesis of Chemistry; II. The Alchemists; III. Qualitative Chemistry; IV. Quantitative Chemistry; V. Structural Chemistry; VI. Special Branches of Chemistry. Each Part is subdivided into unnumbered sections and paragraphs, with headings in bold-faced type, making the book convenient for study.

Considering the limited space in the book, the author has certainly arranged an accurate compendium for chemical students, covering the entire field. He shows knowledge of the standard works on historical chemistry in three languages, but he appears not to have access to the earlier original works, except in a few instances. Viewed in the light of the original writings of the zealous alchemists, the iatro-chemists, and the learned philosophers of the last century, the history of chemistry becomes as fascinating as a romance, and a work based on them acquires an individuality which is only partly reflected in a compilation at second-hand.

We notice that high honor is paid to the erudition of the Arabian chemist, Geber, notwithstanding Berthelot has shown that the writings usually ascribed to Geber can not be traced

back farther than the beginning of the XIII century, and that they never did exist in Arabic; the MSS. said to be found in the Paris Bibliotheque Nationale and which have been translated into Latin and modern languages are fictitious.

In a larger part of the volume the subject is treated in a series of biographies; this, however, is natural where the discoveries of certain individuals exerted radical changes in the philosophy of the science.

In Parts IV and V the development of modern chemistry is well set forth, and every student of the science would do well to read and absorb these chapters early in his curriculum.

Professor Venable names a chemical periodical established as early as 1697 by Stahl.

An excellent feature of the work is its fair-mindedness, giving credit where credit is due. This remark is, perhaps, superfluous, as the book is American; but after Jagnaux' great volumes, written to prove that chemistry is a French science and the polemical writings of certain German authors, one can not but recognize the impartiality characteristic of American writers.

A few illustrations, portraits, and representations of original apparatus would have enlivened the volume; perhaps these can be introduced in a second edition. The proof-reading is excellent. There is an index. H. C. BOLTON.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS. BY DR. ALEXANDER CLASSEN. AUTHORIZED TRANSLATION, SECOND ENGLISH, FROM THE THIRD GERMAN EDITION, REVISED AND GREATLY ENLARGED. BY W. H. HERRICK, A. M. New York: John Wiley & Sons. 1894. Price $3.00.

It is now twelve years since Professor Classen published the first edition of this book. The little volume of about fifty pages contained a systematic description of the methods then practiced in the laboratory at Aachen, little or no attempt being made to include the results that had been obtained elsewhere. An entirely rewritten and much enlarged second edition was issued in 18 6. In this, electrolytic analysis is treated as an independent branch of quantitative analysis, but while the methods proposed and worked out by the author and his associates are fully presented, only occasional reference is made to the researches of

other experimenters: "Nach eignen Methoden," still remained the device of the book.

A third edition, of which the subject of this review is a translation, appeared in 1893. The author now evidently attempts to present a complete treatise on electrolytic analysis. The numerous controversies with other chemists, and the adverse criticism of some of his methods, have induced him to revise and modify considerable portions of the text, and to introduce many methods developed and described by others. Nevertheless the book is not entirely free from the defects of its earlier editions. Especially is it to be regretted that Prof. Classen has not thought it worth his while to give references to the original papers.

The most satisfactory part of the work comprises the introductory chapters; the descriptions of the apparatus used for generating, reducing, and measuring the current are very complete, and leave little to be desired. The Gilcher thermopile might, perhaps, have replaced the older constructions, and some of the obsolete forms of galvanic cells might have been omitted. The translator has made some very judicious additions, describing devices used in American laboratories.

Under "Determination of the Metals" much new matter has been introduced. Great stress is laid upon the proper control of the current, and, whenever possible, the normal density is given. Most of the space is allotted to the precipitation of metals from solutions of their double oxalates, and it is tacitly assumed, that this is in most cases the best method. Prominence is also given to the electrolysis of the sulphosalts of antimony and tin—a method improved by Classen—and the deposition of metals from solutions of their pyrophosphates (Brand). The names of Smith and Rüdorff appear very frequently, but we do not find that the directions for carrying out their processes are always adequate, and not a few of the American chemists' methods are entirely omitted.

This criticism applies even more strongly to the section on the separation of the metals. While excellent results are doubtless to be obtained by the use of many of the methods described here, it can not be denied that some are not separations at all (iron from cobalt, nickel, and zinc, etc.), and others are not

electrolytic separations. It seems to us that in many cases the author could have substituted, with advantage, the electrolytic processes, which have been proposed by others in recent years.

Professor Herrick's translation is excellent in every respect; while it closely follows the original text, it contains numerous very valuable additions. H. F. KELLER.

LABORATORY MANUAL AND PRINCIPLES OF CHEMISTRY FOR BEGINNERS. By GEORGE M. RICHARDSON, ASSOCIATE PROFESSOR OF CHEMISTRY IN THE LELAND STANFORD JUNIOR UNIVERSITY. pp. 233. New York: Macmillan & Co. 1894. Price $1.10.

This book is, as the author states in his preface, "principally intended as a *laboratory manual*," and the course of experiments "arranged for the elementary students of chemistry in this university." It is in two parts, Part I (pp. 84) consisting of a course of laboratory experiments, and Part II being devoted to theoretical chemistry.

While many of the laboratory experiments contained in Part I are instructive and well adapted for their purpose, and well suited for beginners, there are also many with which fault may be found.

In some instances these experiments involve the use of rather complicated pieces of apparatus requiring an expenditure of the student's time to get together and set up which is out of proportion to the importance of the fact to be taught by the experiment itself; in other instances the time and work required to perform the experiment are in like manner excessive when taken in comparison with the importance of its object.

But a far more serious fault than this lies in the difficulty of most of the quantitative experiments, of which there is a very considerable number, "greater," as the author states, "than is commonly found in such laboratory manuals."

Most of these quantitative experiments are decidedly beyond the ability of the average beginner in chemistry to perform with any degree of accuracy, and some of them can yield accurate results only in skilled hands.

It is far worse than useless to require a student to perform quantitative experiments without also requiring of him accurate results; hence, if quantitative work is to be given to the beginner

at all; in itself a matter of more than doubtful expediency; the experiments given him should be of the simplest kind only, and of such a nature that even in inexperienced hands, fairly accurate results may be obtained.

The requirement from students of quantitative work, the proper performance of which lies beyond their abilities, is almost inevitably followed by one of two consequences—the conscientious student, failing after repeated attempts to obtain correct results from an experiment, is apt to become discouraged, and begins to dislike his work; his less conscientious fellow, tiring of an experiment after he has repeated it once or twice, "cooks" his figures to give the desired result in order to get rid of it. In either case the harm done is great.

In Part II, "the writer has attempted to give a clear and concise statement of some of the fundamental theories and principles of chemistry; here he has gone more into detail than is customary in books designed for elemetary students."

This part is open to a similar criticism. Some of the matter it contains might be read with advantage by a beginner, but it is not in such form as to be readily available, and the consideration of such subjects as Absolute Temperature, The Determination of Molecular and Atomic Weights, The Determination of Formulas, The Kinetic Theory of Gases, etc., can scarcely be undertaken with profit by beginners in chemistry, and is also rather out of place in a book "principally intended as a laboratory manual."

On the whole, while with some revision the book would be an excellent one to place in the hands of a second-year student, it is hardly one which can be recommended for the use of beginners.

R. D. C.

NOTES.

International Chemical Congresses.—The following circular letter has been addressed to the foreign chemical societies:

DEAR SIR:

An International Congress of Chemists, organized in connection with the World's Columbian Exposition, was held at Chicago in August, 1893. The American Chemical Society met

conjointly with the Congress, and, on account of the interest which was manifested, appointed a Committee of Conference to consider the expediency of holding similar congresses at regularly recurrent intervals of time. The geologists have established a series of International Congresses, which meet triennially; in medicine and pharmacy similar organizations exist; and in each case the success of the meetings has been very great. The undersigned, therefore, representing the American Chemical Society, respectfully request the chemical societies of the world to appoint similar committees of conference, in order to consider whether it is desirable and practicable to organize a series of International Chemical Congresses, in which the chemists of the various nations can regularly meet together for the discussion of questions of common interest. Hoping for a favorable response, we remain, in behalf of the American Chemical Society,

Very respectfully,

(Signed,) F. W. CLARKE,
CHARLES E. MUNROE,
H. CARRINGTON BOLTON,
EDWARD HART,
W. O. ATWATER.

Please address reply to F. W. Clarke, U. S. Geological Survey, Washington, D. C., U. S. A.

Soldering Aluminum.—Professor Joseph Richards contributes an article on this subject to the first number of the *Aluminum World* from which we learn that the best results have been obtained from an alloy of zinc, tin, aluminum and *phosphorus*. "This solder can be used before the blowpipe or with a soldering iron. In the former case, a little silver can be added to it without making it too hard to melt, and giving it a better color. For use with the copper bolt, this solder leaves little to be desired. The surfaces to be united are first scraped clean, and then tinned with the solder itself by rubbing it on hard with the bolt. The prepared edges are then soldered together with ease, using a hot iron and no flux of any description."

Pure tin, or an alloy of tin and aluminum will solder, but the joints become brittle. Zinc and cadmium are useless because too brittle. Silver chloride attacks aluminum depositing silver,

and the surfaces thus formed may be soldered, but the material is too costly. Cadmium chloride can be used only when dry, and is a deliquescent salt. The Alsite aluminum solder is used only with the blowpipe; its composition is not divulged, and the melting-point is dangerously near that of aluminum. Electroplating the surfaces to be soldered is not satisfactory as the plating peels when subjected to heat. E. H.

Note on a Device for Weighing Oil for Analysis.—The following device I have for some time used, and found to be so convenient and simple, that I give a description of it hoping that it may be of service to others. It consists simply of a small glass evaporating dish, about one inch in diameter, supported upon a flat watch-glass. An amount of oil, greater than the amount desired for the experiment, is placed in the evaporating dish and the whole weighed. The proper amount of oil is then poured from the dish into the vessel in which it is to be analyzed, and its weight determined by difference. If a drop of oil should cling to the lip of the evaporating dish and run down on the outside, it will be caught by the watch-glass and will occasion no trouble. The whole affair costs but a few cents and may be cleaned with great ease, while for weighing oil it is quite as accurate as a weighing pipette.

November 5, 1894. PARKER C. MCILHINEY.

ERRATA.—Page 348, May, 1894, ninth line from top of page, after the words *violent bumping*, insert *ninety cc. of water is now added.*

Page 349, May, 1894, in the last two lines, for *Cengola* read *Angola.*

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Proceedings.

JULY 28, 1894.

In view of the fact that some members seem dissatisfied with certain provisions of the Constitution the President has been authorized by Council to appoint a committee to consider suggestions in regard to amendments to the Constitution of the Society.

NEW MEMBERS ELECTED JULY 17.

Anderson, J. T., Auburn, Ala.
Graham, W. H., 350 Central Ave., East Orange, N. J.
Hare, C. L., Auburn, Ala.
Kilmer, F. B., New Brunswick, N. J.
Lee, Isaac A., 162 Somerset St., New Brunswick, N. J.
McIlhiney, Parker C., School of Mines, Columbia College, New York, N. Y.
Miller, H. K., Auburn, Ala.
Noble, R. E., Auburn, Ala.
Parmly, Dalton, Oceanic, N. J.
Persons, Prof. A. A., Lake City, Fla.
Roeser, Frederick, care Globe Sm. and Ref. Co., Denver, Colo.
Slate, Wm. W., Bellows Falls, Vt.
Street, John Phillips, New Brunswick, N. J.
Taylor Duncan, care of Colgate and Co., Jersey City, N. J.

CHANGE OF ADDRESS.

Andrews, F. H., Box 476, Providence, R. I.
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Bouton, Rosa, Chem. Dep't., State Univ., Lincoln, Neb.
Crobaugh, Frank L., No. 17 Bratenahl Building, Cleveland, Ohio.
Dohme, A. R. L., 301–307 W. Pratt St., Baltimore, Md.
Dorr, John V. N., Polytechnic Institute, Brooklyn, N. Y.
Drew, Dr. Chas. W., 505 Century Building, Minneapolis, Minn.

Dunham, E. K., 358 E. 26th St., New York, N. Y.
Eager, F. D., Savoy, Neb.
Emmens, Stephen H., Amador City, Amador Co., Cal.
Escher, Paul, 212 E. Onondaga St., Syracuse, N. Y.
Farnsworth, John P., 26 Tobey St., Providence, R. I.
Ford, Allen P., 254 24th St., Detroit, Mich.
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Genth, F. A., Jr., 103 N. Front St., Philadelphia, Pa.
Goodell, F. E., 1420 W. 12th St., Des Moines, Ia.
Hahn, A. G. C., 4 and 6 New Chambers St., New York, N. Y.
Harrington, E. M., Aetna, Lake Co., Ind.
Hawling, Henry H., 2135 L St., Washington, D. C.
Hays, Joseph A., care of E. M. Johnson Co., 98 William St., New York, N. Y.
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Meeds, Alonzo D., Stillwater, Minn.
Menges, Franklin, Ph. D., Gettysburg College, Gettysburg, Pa.
Miller, John A., 203 Ellicott St., Buffalo, N. Y.
Mitting, E. K., 416 Huron St., Chicago, Ill.
Parmly Dalton, Sharpsville, Pa.
Quinan, Wm. R., Pinole, Contra Costa Co., Cal.
Richards, Joseph W., Ph. D., Lehigh Univ., Bethlehem, Pa.
Schiller, Louis J., Granite St., Am. Sug. and Ref. Co., So. Boston, Mass.
Voorhees, Louis A., Box 290, New Brunswick, N. J.
Willard, J. T.. Kan. State Agr. Coll., Manhattan, Kan.
Williams, W. J., 1412 Van Buren St., Wilmington, Del.
Wyckoff, George H., 1233 Washington, St., Kansas City, Mo.
Yount, Clarence E., 20 6th St., S. E., Washington, D. C.

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THE BROOKLYN MEETING.

AUGUST 15 AND 16, 1894.

THE Brooklyn meeting was a very interesting one. The attendance was large, the papers numerous and interesting, and the excursions and social features successful and enjoyable.

The meeting was opened in the Chemical Lecture Room of the Brooklyn Polytechnic Institute on Wednesday, August 15, at 10 A. M., by Dr. Wm. McMurtrie, Chairman of the Committee of Arrangements, who briefly stated what arrangements had been made, and welcomed the visiting chemists. After a brief response by President H. W. Wiley, the Secretary made some announcements and stated that 728 names were now on the roll of members, and that of these only thirty-eight had not paid dues for the current year.

Dr. Wm. H. Hale presented through the Secretary, on behalf of the street railway companies, 500 trolley tickets for the use of members, for which a vote of thanks was passed.

The following papers were then read and discussed:

Contributions to the Chemistry of Cerium.
L. M. DENNIS and W. H. MAGEE.

Utilization of Acid Sulphates, particularly the so-called Niter Cake of the Trade ..... JOHN ENEQUIST.

Oxidation of Non-drying Oils by Air ..... WALTER D. FIELD.

Oil-Gas ..... W. A. NOYES.

Determination of Benzene in Illuminating Gas ..... W. A. NOYES.

The Secretary announced that Dr. Wolcott Gibbs had been unanimously nominated by the Council for election to honorary membership in the society. Upon motion of Prof. C. E. Munroe, Dr. Gibbs was unanimously elected to honorary membership by a rising vote and the Secretary was directed to inform Dr. Gibbs of this action by telegraph.

The editor was called on for information about the JOURNAL and stated that considerably over 900 copies were now being sent out, only a few being exchanges. Probably 875 of these copies represent paid subscriptions, either of members or non-members. The number of subscribers who are not members is large and growing. The JOURNAL has been enlarged to seventy-two pages, and it has become necessary to reprint the January,

February, and March numbers, the first edition having been exhausted. A considerable amount of copy was now on hand and it would probably be necessary to still further enlarge the JOURNAL before the close of the year. Some further improvements were in contemplation but not yet ready for announcement. The greatest difficulty in the way of the Committee on Papers and Publications was in the lack of sufficient funds to print the material which came to the editor. He ventured to hope that members would bestir themselves in inducing proper persons to become members of the Society.

The President congratulated the members of the Society upon the good showing made. A charter for a Local Section had just been granted to the New Orleans chemists, and another section was in process of formation in San Francisco. With the present rate of increase the membership would doubtless exceed 1,000 before the close of the year. Chemistry has a great future in America. There is every reason to think that with proper effort we may have in this country the greatest chemical society the world has ever seen.

In the afternoon an excursion on the steamer "Blackbird" through the East river and adjacent parts of Long Island Sound had been arranged by the local committee. Stops were made at the Mineral Water Manufactory of Mr. Carl H. Schultz, 430–440 First Avenue, New York.

The party was met on the dock by Dr. Schultz and Dr. Hallock, who escorted them to the factory. After doing justice to a luncheon, served by Delmonico, the members were shown through the works by Dr. Schultz, Dr. Hallock, chemist, and Mr. Louis Waefelaer, mechanical engineer.

Established in 1862, these works have now grown to enormous proportions. The factory building is a substantial brick structure, four and five stories in height, covering half a city block. The factory is divided into nineteen departments:

Boiler rooms, engine rooms, siphon-testing department, gas-generating department, buffing department, siphon-filling department, bottle-filling department, pumping station, refrigerating department, water-purifying department, distilling department, cooling department, storage department, chemical department, foundry department, machine shop, electroplating department, carpenter shop, stables.

The carbon dioxide used in the water is generated in heavy lead-lined copper cylinders, from ground dolomite and sulphuric acid, after which it passes through a set of coolers, washers and purifiers to completely remove all impurities. It is stored in a gas-holder, from which it is

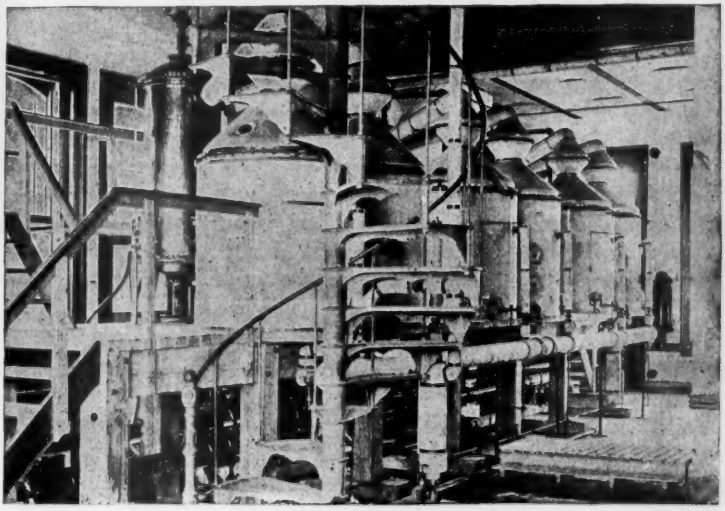
drawn for use in the siphon-filling machines, or compressed in large iron tanks to be used in charging the water in bottles or fountains.

In the building situated on First avenue, are placed the siphon-filling rooms. The solutions containing the numerous ingredients necessary for the production of a correct mineral water are first prepared from standard solutions in the laboratory, and sent over to the siphon-filling department and introduced into large marked vessels. These vessels are filled up to the mark with cold distilled water and thoroughly mixed with a stream of carbon dioxide. Two samples are taken, one from the top and the other from the bottom of the tank, and sent to the laboratory for examination. No siphons can be filled from a solution until it has been examined by the chemist and found to be correct.

The solution flows into a pail, and from this pail it is pumped into the machine. The pump takes the solution in on one side, and the gas in on the other; after compressing the gas into the water, the charged water is forced into a cylinder or reservoir on the top of the machine, from which it is conducted to the siphon.

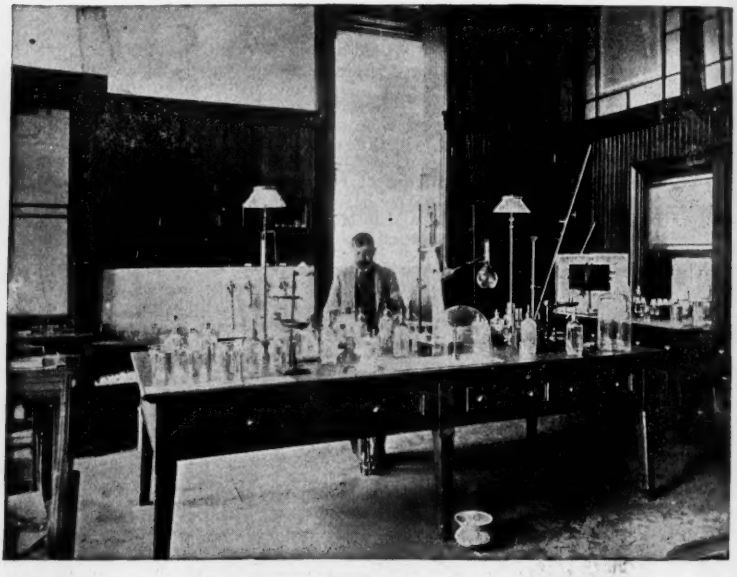
After many costly experiments Dr. Schultz found that the only way to obtain a pure and tasteless distilled water, was to thoroughly remove all impurities before distilling. In order to remove all suspended matter, the water is pumped through an ingenious filter invented and patented by his deceased son Carl H. Schultz, Jr. It consists of a large vessel suspended on trunnions which can be easily inverted, quickly washed out and afterwards sterilized with live steam, which not only thoroughly cleanses the filtering media, but destroys all organic growth, which has been the great objection to the use of filters. These filters are cleaned and sterilized every day. In the basement are also the boilers, refrigerating machine, cooling coils and hoisting machinery.

The croton water used is pumped in from the street mains and through



DISTILLING APPARATUS.

the sterilizing filter. Then it passes up-stairs through a set of heat exchangers, which are upright tin-lined copper cylinders containing a large number of one-inch pipes. Here it meets the hot distilled water coming down, thereby cooling the distilled water and heating up the filtered water. On the top floor the water is heated up as much as possible with exhaust steam from the ice machine, then boiled with live steam to drive off the volatile organic matter, the steam being drawn off with an exhaust fan and thrown away. After the removal of the volatile organic matter, the water flows down into the feed-boxes which are constructed to maintain a constant level of water in the stills. The stills, six in number, are arranged in three sets of two each. They are constructed of heavy copper, thoroughly tinned inside. They are about three feet in diameter and four feet in height, surmounted with a dome and separator to prevent any solid particles from being carried over with the steam. They are provided with water and steam gauges, two hand-



ANALYTICAL LABORATORY.

holes on each side for cleaning, and two glass peep-holes on opposite sides on the top. In front of one of the holes a gas-jet is kept burning, which furnishes light to the inside of the still.

The condensation of the steam for distilled water, takes place in tall vertical cylinders, containing a large number of small pipes, through which the cooling water is pumped. Only one condenser is required for two stills. The large amount of cooling effect is obtained indirectly from river water, and to guard against contamination which would result from the river water getting into the distilled water, only croton water

is run through the condensers, and this hot water cooled down for use again by pumping it through a series of coils, over which a stream of river water is kept constantly running.

The distillation is accomplished by steam supplied from two large steam boilers. This steam, which is still very hot when it leaves the still, is conducted to the top floor and used for preheating the water before distillation, thereby utilizing all the heat.

The hot distilled water after leaving the condensers passes down through a set of heat exchangers where it is cooled down as much as possible by the filtered croton water, and then through a second set where it is cooled down to about 40° F. by cold water from the refrigerating machine. It is then stored cold in large covered tanks provided with cotton-plugged vents to prevent any contamination from the air. All the apparatus is constructed of heavily tinned copper, the conducting pipes are made of block-tin and all the valves are silver-plated to guard against any possible metallic contamination.

On the second floor are the laboratories. They consist of two large rooms where the solutions are prepared, and two smaller rooms for analytical work. One of these rooms is especially fitted up for water analysis, and bacteriological work; besides these, there is a small dark room for spectrum analysis and photographic investigation.

The walls are hard finished and painted, and all around is a white pine wainscoting of narrow boards about eight feet high, leaving a space of about three inches from the wall; in this space the water and gas pipes are placed so as not to be seen. The wainscoting is built in sections so any section can be removed, in case it is necessary to get at the pipes for repairs. In the upper part of the partitions are large ground-glass fanlights which can be opened when extra ventilation is required. The doors have large panels of chipped glass with the names of the different departments cut in. The hood and around the sinks are lined with white tile, giving it a neat appearance, and can easily be kept clean. The front is entirely taken up with large windows furnishing plenty of north light and ample ventilation even in the warmest weather.

The laboratory is well-equipped with all the necessary apparatus, for Dr. Hallock is one of the few fortunate chemists whose employer is generous enough to give him *carte-blanche*.

The luncheon served by Delmonico was unique and deserves special mention. The only appropriate adjective that can adequately describe it is, superb. A pleasant feature was the figures of chemical apparatus with appropriate mottoes designed by Dr. Hallock. One of these represented two retorts with crossed necks and the inscription: "Treat with an excess of C_2H_5OH," another a picture of a liter flask inscribed, "Fill up to the holding mark."

In returning thanks Dr. Wiley remarked that his idea of the term "mineral waters" had been much enlarged. At the morning session he had suggested that he was not accustomed to lunch on mineral water. That remark he now wished to withdraw entirely. Mr. Schultz responded.

Returning to the steamer the party proceeded to Willet's

Point, where they were welcomed by Colonel King and staff. The visitors were shown an immense electro-magnet, made by using one of the old Rodman guns as a core, and three torpedoes were exploded and photographed. The party then inspected the Museum of Engineering Models and reviewed the parade.

The officers, twenty-five in number, are West Point graduates. There are 425 enlisted men also stationed here. The officers follow the course laid down in the school schedule, while the men are drilled and instructed in the various duties of engineer troops.

THURSDAY, AUGUST 16.

Papers read and discussed:

Note on the Hardening of Mortar.....WILLIAM P. MASON.

Note on the Test for Strychnine.....WILLIAM P. MASON.

The Quality of Water Supplies.....WILLIAM P. MASON.

The Bacteriology of the Soil as Affected by Depth, Character and Use.....LUCIUS PITKIN.

Report on Abbreviations of the Names of Metric Terms Used by Chemists.....WM. H. SEAMAN.

Some Points in Making Molybdate of Ammonia Solutions for Phosphorus Determinations.....CHARLES B. DUDLEY.

Ucuhuba Fat.....JOSEPH F. GEISLER.

[This paper was read by title in the absence of the author.]

A New and Rapid Method of Estimating the Total Proteids in Milk.....E. H. BARTLEY.

At this point the session was adjourned in order that the members might be free to attend the meeting of Section C., of the American Association for the Advancement of Science, to listen to the address by Vice-President T. H. Norton.

At the adjourned session the following papers were read:

Inspection of Cotton for Use in Gun-Cotton Manufacture.
CHAS. E. MUNROE.

Ferric Acid and the Ferrates.....C. A. O. ROSELL.

After a vote of thanks to Dr. E. R. Squibb and Sons, Edward Smith and Co., Carl H. Schultz, Dr. A. P. Hallock, Col. W. H. King, Willet's Point, Mr. Wolf, Disinfecting Plant, Riker's Island, The Long Island Brewery, The Hygienic Ice Co., The Standard Oil Co., The Bergen Point Chemical Works, The Fogarty Gas Co., The Balbach Smelting and Refining Co.,

Feigenspan's Brewery, and the Trustees and Faculty of the Brooklyn Polytechnic Institute, the meeting adjourned.

THURSDAY AFTERNOON.

Some forty or fifty of the chemists visited the Vacuum brewing and the ice-making plants. At the brewing works they were shown through vault after vault full of immense casks of the "Lager," were given a lunch and shown the apparatus for cooling the beer and for forcing carbonic acid gas through it after the fermentation, since by the vacuum method not enough of the gas was formed in it.

At the ice works they were shown the whole process in so far as it could be easily seen: the pumps, the cans in which the water was frozen, with the various stages of the operation which requires about three and a half days for completion, the method of taking the ice cakes out of the cans, etc.

At various times during the meetings, parties of chemists visited the works of Dr. E. R. Squibb and Sons and Edward Smith and Co.

The factory of E. R. Squibb and Sons, for the manufacture of acetic acid and acetates, is a large plant at the foot of Gold street, on the East river water front of Brooklyn. The plant is divided into wood yard on the water front and factory proper in the rear. First were shown the machinery and appliances for cutting up the wood into small billets. Then the loading of this cut wood into iron retorts or cars which run on elevated tracks by means of winches. By these tracks the cars are run into and out of air-bath cells for the distillation of the wood. Each car or retort holds about 2.8 cords of wood, and each oven has twelve cells for as many cars, and the firing and draft flues pass under the floors of the cells, so that the combustion of fuel and its products do not get contact with the retorts or cars of wood. Each retort or car has an eduction pipe which passes through the rear wall of the cell and is connected with a large Liebig condenser. The distillation is conducted at temperatures below 204° C. (400° F.) of the air-bath and the process requires about seven days for each retort. The first day yields water only. Then comes very weak crude acetic acid, and the strength slowly and steadily increases up to about twenty-five per cent. This crude, smoky acid contains but little tar, and when saturated with soda-ash the salt is dried and heated until nearly anhydrous. It is then decomposed with two equivalents of sulphuric acid in a still of peculiar construction with a mechanical stirrer, and yields very strong acetic acid of good quality. This acid is then rectified from bronze stills through glass or silver condensers, yielding the various strengths of fine acid. The commercial grades of acid of different strengths for use in the arts, are made in large stills of ordinary construction from commercial calcium acetate of the markets: decomposed with sulfuric or hydrochloric acid.

The wood after distillation is allowed to cool in the retorts and is then dumped and put up in bags of fifty pounds each, and sold to railroads, steamboats, fire departments, etc., as a kindling material for coal, being

itself an almost perfect fuel, easily lighted, and efficient in very small quantity.

This factory is under the management of Mr. Charles F. Squibb, who was always ready to show it to any of the members of the Society sufficiently interested to accept the invitation of the firm.

The pharmaceutical laboratory was shown to those who visited it during the meeting, chiefly by Dr. E. H. Squibb, who now relieves his father in the management of that part of the business of the firm. It is a large building of five stories, built around a central court yard, and the general plan is to manufacture in the upper stories, store and fill in the next lower, and finish and stock in the next lower, while the ground floor is used for offices, shipping, storage of material, etc. The basement contains the boilers, engines, mills, pumps, drying hoods, etc. The ether apparatus occupies a detached section of the building three stories high, and is fire-proof like many of the other parts. The building is supplied throughout with good apparatus and fixtures too complicated and varied to be comprehended in a short visit, and both apparatus and workmen were clean and orderly. Everything was freely shown and all questions were freely and frankly answered in accordance with the long-established policy of E. R. Squibb and the present policy of E. R. Squibb and Sons.

At the factory of Edward Smith and Co. were seen: First, supplies of raw material; all the commonly known kinds of copal resins, both fossil and recent; also dammar and shellac; linseed oil both raw and prepared for use; refined turpentine having a constant boiling-point, and the still used in redistilling it; the utensils and plant employed in varnish-making, with the operations actually going on; the testing of the finished goods; the most recent improvements in mills, etc., for grinding pigments in varnish and japan; the technical chemical laboratory; and in general, the methods in common use for the management of the manufacturing part of the varnish business. There were to be seen a very large collection of samples of resins and oils, and the kettle in which was made the first batch of varnish ever made in America, besides some old Dutch varnish kettles more than forty years old and still in use.

On Saturday, 18th, the party visited the Standard Oil Works and the Bergen Point Chemical Works at Bayonne, and the Balbach Smelting and Refining Works and Feigenspan's brewery at Newark. This was a joint excursion with Section C. of the American Association for the Advancement of Science. The following account written by one of the party, is abbreviated from one of the Brooklyn daily papers.

The sail down New York Bay was a charming one. The temperature was just right, the atmosphere was clear and the refreshing breeze invigorating.

The first works inspected were the refineries of the Standard Oil Company at Bayonne. The chemists were given every opportunity to inspect the plant, and the processes were carefully explained by the manager, Mr. Van Winkle. The oil comes in through two six-inch pipes, and is started from the pumps under a pressure of about twelve hundred pounds. From the receiving tanks the oil is pumped into a number of stills, each having a capacity of 600 barrels. The products obtained from these stills are a light naphtha, heavy naphtha, white oil, distillate and slops in the order given. The white oil is sold for illuminating purposes,

and the distillate is refined by treatment with acids before it is used for illumination.

It takes three days to run off a "charge" from one of these stills, and it is then thoroughly cleaned before being charged again.

The tarry residue from these stills is treated for lubricating oil and paraffin being pressed through canvas at a temperature of 60° to 65° F., and that which runs out being again subjected to pressure at a much lower temperature.

The distillate from the stills is treated with sulphuric acid, then with steam in an agitator, then with soda and washed to fit it for the market.

After the sludge acid is removed from the tarry product a porous, nearly pure carbon is left which is sold, much of it being used to make the carbon pencils for electric arc lights.

The next visit was to the Bergen Point Chemical Works near by. Here sulphuric acid is made from iron pyrites, and the sludge acid from the Standard Oil Company's Works is refined.

At the Balbach Works, lead ore carrying silver, gold and other metals, is received by steamer from Mexico, and, after treatment, the refined products are shipped to the European market.

The ore is roasted in a reverberatory furnace to remove first the copper and then the antimony as dross.

After these are removed it is put into the softening furnace where other impurities are driven off, and it is then treated by the Parke process for separating the silver and gold from the lead.

The silver, gold, zinc, and some of the lead rise up to the surface and are skimmed off together to be separated from one another by further processes, that which remains being lead, carrying a little zinc and other impurities. This is refined and the pure lead is then ready for the market.

The skimmings from the Parke process are first heated in a crucible of plumbago to drive off the zinc, which comes off as a vapor. This vapor is condensed to liquid zinc, which is run into moulds and allowed to cool.

Silver, lead and gold are then passed on to the crucible by dumping the latter. After cooling, the mass is transferred to a cupel, where it is again melted and a current of air passing over the molten surface changes the lead to litharge which floats upon the surface and is drawn off, leaving the pure silver and gold.

To separate the silver from the gold the combined metals are treated with hot sulphuric acid, which dissolves the silver but does not attack the gold. The silver sulphate thus formed is transferred to a vat in which are placed thin plates of copper. By this means the silver is deposited in the pure metallic state and the copper goes into solution, and is sold to be used in making crystals of copper sulphate.

Many other processes of interest were shown, such as methods of sampling and assaying, charging the blast-furnace, treating the various slags and dross.

The last visit of the day was that to the Feigenspan brewery in Newark, which proved a most interesting part of the day's excursion.

The Board of Directors have granted a charter for a Local Section in New Orleans and vicinity.

MEMBERS PRESENT.

H. W. Wiley.
C. F. McKenna.
F. E. Dodge.
Wm. Frear.
S. A. Lattimore.
Alfred Springer.
Charles E. Munroe.
A. A. Breneman.
E. H. S. Bailey.
Ernest Ellsworth Smith.
L. M. Dennis.
Ferd. A. Sieker.
Albert H. Welles.
Rosa Bouton.
R. G. Eccles.
Henry Souther.
W. A. Noyes.
Jos. A. Hays.
R. W. Cornelison.
William Coutie.
Frederick J. Wulling.
Owen Louis Shinn.
John Enequist.
Lyman B. Hall.
Chas. Baskerville.
Peter T. Austen.
Walter M. Saunders.
Herman G. Schanche.
F. A. Flückiger.
G. C. Caldwell.
Edward B. Voorhees.
Herbert B. Baldwin.
Frank H. Andrews.
Frederick G. Zinsser.
Leo Baekeland.
W. S. Myers.
Dalton Parmly.
T. Lyndon Briggs.
W. Ernest Wadman.
A. H. Sabin.
W. P. Mason.
Walter D. Field.
Francis J. Oakes, Jr.
G. G. Pond.
A. P. Hallock.
E. H. Squibb.
H. Endemann.
Frederic Read.
Herbert S. Bird.
H. N. Stiles.
Charles T. Pomeroy.
S. P. Mulliken.
Mrs. Lyman F. Kebler.
G. J. Volckening,
E. H. Bartley.
T. H. Norton.
W. H. Chandler.
Albert C. Hale.
Edward Hart.
C. Wellington.
M. A. Scovell.
Wm. McMurtrie.
Edgar F. Smith.
Francis C. Phillips.
Wm. H. Seaman.
F. W. Spanutius.
Joseph A. Deghuée
George Archbold.
W. B. Landon.
Edward J. Fuchs.
W. M. Grosvenor, Jr.
F. W. Mar.
R. B. F. Randolph.
C. E. Munsell.
Augustus H. Gill.
Chas. W. Moulton.
Mary Coutie Clark.
Sidney S. Emery.
E. A. de Schweinitz.
J. H. Wainwright.
John. A. Myers.
Robert Hall.
Frank Schoney.
Mary Engle Pennington
Frederick B. Power.
Charles H. Herty.
H. Pennington.
John C. Hebden.
S. A. Goldschmidt.
E. R. Squibb.
E. D. Williams.
C. Chauncey Parsons.
F. S. Hyde.
Franklin Menges.
Parker C. McIlhiney.
C. B. Cochran.
F. Hemburg.
Otis C. Johnson.
W. H. Graham.
Frank Julian.
W. M. Stiles.
Loomis Burrell.
Marcus Benjamin.
Francis J. Oakes.
G. Gehring.
A. G. C. Hahn.
Carl H. Schultz.
Mrs. E. R. Squibb.
M. Alsberg.
Lucius Pitkin.
C. L. Speyers.
Jas. Lewis Howe.
J. W. Provine.
Lyman F. Kebler.
Elwyn Waller.
W. S. Johnson.
Woodville Latham.
Peter O. Terheun.
Morris Loeb.
Henry A. Mott.
Chas. B. Dudley.
J. S. Stillwell.
W. Goold Levison.
Wm. R. Christmas.

Issued with November Number, 1894.

Proceedings.

By vote of the Council the Winter meeting will be held in Boston, Dec. 27 and 28, 1894.

Authors of papers intended for this meeting should forward their manuscript to the Secretary, Prof. Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y., as soon as possible.

Notice is hereby given that no paper can be read, except by unanimous consent, unless it has first been submitted to the committee on Papers and Publications. In order that this committee may pass upon communications intelligently they should be sent to Prof. Hale at as early a date as possible.

The Council has accepted the resignation of Dr. H. Carrington Bolton as a member of the Board of Directors.

NEW MEMBERS ELECTED OCTOBER 9.

Burn, E. C., 1722 Vallejo St., San Francisco, Cal.
Burrell, Loomis, Little Falls, N. Y.
Eccles, Dr. Robert G., 191 Dean St., Brooklyn, N. Y.
Fisher, Davenport, 718 Cass St., Milwaukee, Wis.
Herrick, Wm. Hale, 54 Vessey St., New York, N. Y.
Hershey, Aldus N., Waynesboro, Franklin Co., Pa.
Latham, Woodville, 18th St. and 3d Ave., New York, N. Y.
Parsons, C. Chauncey, 43 Sedgwick St., Brooklyn, N. Y.
Power, Frederick B., Fritzsche Bros., 34 Barclay St., New York, N. Y.
Volckening, Gustave J., 675 Lafayette Ave., Brooklyn, N. Y.
Wiltberger, F. K. I., Alexandria, Va.

CHANGES OF ADDRESS.

Buchanan, Dr. C. M., 918 Virginia Ave., S. W., Washington, D. C.
Breyer, Dr. Theodor, 511 Linn St., Peoria, Ill.

De Chalmot, G., Johns Hopkins Univ., Baltimore, Md.
Escher, Paul, care of Solvay Process Co., Syracuse, N. Y.,
Falkenau, Louis, 434 California St., San Francisco, Cal.
Graham, Wm. H., 350 Central Ave., East Orange, N. J.
Grosvenor, W. M., Jr., Box 166, Johns Hopkins Univ., Baltimore, Md.
Julian, Frank, care of Ill. Steel Co., South Chicago, Ill.
Lammers, T. L., Townsend, Montana.
Lee, C. T., 146 Franklin St., Boston, Mass.
McCurdy, Chas. W., Univ. of Idaho, Moscow, Idaho.
Meeds, A. D., 427 12th Ave., S. E., Minneapolis, Minn.
Munsell, Dr. C. E., 113 Henry St., Brooklyn, N. Y.
Roth, D. M., Ingleside Place, Walnut Hills, Cincinnati, Ohio.
Saarbach, Ludwig, Ph. D., 12 Old Slip, New York, N. Y.
Schanche, Herman G., P. O. Box 149, Darby, Pa.
Smith, Alex., Univ. of Chicago, Chicago, Ill.
Smith, E. E., 157 E. 14th St., New York, N. Y.
Smith, Edward L., 718 Main St., Worcester, Mass.
Smith, Francis P., Chemist U. S. Navy Yard, New York, N. Y.
Sohon, M. D., Johns Hopkins Univ., Baltimore, Md.
Stokes, H. N., U. S. Geological Survey, Washington, D. C.
Voorhees, Louis A., Box 290, New Brunswick, N. J.
Wyckoff, Geo. H., care of Curtice Bros. Co., Rochester, N. Y.

Issued with December Number, 1894.

Proceedings.

OCTOBER 31, 1894.

The General Secretary has been authorized to collect the dues as heretofore, and retain ten per cent. as his compensation.

C. E. Munroe has been elected a member of the Board of Directors in place of H. Carrington Bolton, resigned.

NEW MEMBERS ELECTED OCTOBER 30.

Bogert, Marston T., Flushing, Queens Co., N. Y.
Cleveland, W. P., care of Empire Zinc Co., Joplin, Mo.
Haines, Joseph E., Mickleton, N. J.
Hand, Daniel, 41 Fulton St., Newark, N. J.
Kenan, W. R., Jr., Wilmington, N. C.
McDermott, Thomas E., S. B., care Kavanagh & McDermott, Washington Ave., above 20th St., Philadelphia, Pa.
Riggs, Louis W., Ph.D., Loomis Laboratory, East 26th St., New York, N. Y.
Weston, Robert Spurr, Cinclare Central Factory, Brusly Landing, La.

ELECTED NOVEMBER 10.

Bell, J. Malseed, M.D., 104 North 7th St., St. Joseph, Mo.
Böhm, L. K., 115 Nassau St., New York, N. Y.
Campbell, George F., 47 North Sheffield Hall, Yale University, New Haven, Conn.
Dabney, Chas. W., Jr., Department of Agriculture, Washington, D. C.
Eyster, Geo. S., Ph.D., 19 Central St., Boston, Mass.
Feid, George F., care Wm. S. Merrell Chem. Co., Cincinnati, Ohio.
Hamburger, Avon, North Wales, Montgomery Co., Pa.
Hoffer, John, Jr., 24 North 2nd St., Harrisburg, Pa.
James, Charles, Tacony, Philadelphia, Pa.
Kedzie, Frank S., M.S., Agricultural College, Mich.
McPherson, Wm., Ohio State University, Columbus, Ohio.
Moody, Herbert R., Mass. Inst. Tech., Boston, Mass.
Pitman, Major John, Frankford Arsenal, Philadelphia, Pa.
Sanborn, J. E., Pottstown, Pa.
Schimpf, Henry W., Ph.G., Brooklyn College of Pharmacy, Brooklyn, N. Y.
Stephens, Henry M., Dickinson College, Carlisle, Pa.
Swan, John N., Ph.D., Monmouth College, Monmouth, Ill.
Talbot, Henry P., Mass. Inst. Tech., Boston, Mass.
Van Ingen, D. A., 135 Henry St., Brooklyn, N. Y.
Wedderburn, Augustus, 1420 Penna. Ave., Washington, D. C.

ELECTED NOVEMBER 20.

Bryan, A. Hugh, 748 North Illinois St., Indianapolis, Ind.
Forbes, Fred. B., Experiment Station, Lawrence, Mass.
Hamilton, W. J., care Pueblo Smelting and Refining Co., Pueblo, Col.
Hartman, Prof. Robert, Ph.D., Missionary Institute, Selings Grove, Pa.
Jones, Walter, Ph.D., Purdue University, Lafayette, Ind.
Patterson, Chas. W., 2421 Dearborn St., Chicago, Ill.
Wallace, W. G., B.S., The Globe Soap Works, Cincinnati, Ohio.
Whitfield, J. Edward, 406 Locust St., Philadelphia, Pa.
Wightman, Hugo, 2421 Dearborn St., Chicago, Ill.,
Yardley, Samuel S., Stevens Institute, Hoboken, N. J.
Unger, T. S., care Carnegie Steel Co., Munhall, Allegheny Co., Pa.

ASSOCIATES ELECTED OCTOBER 30.

Atkinson, Elizabeth A., Three Tuns, Pa.
McCready, Ernest B., Easton, Pa.
Wetmore, L. L., Englewood, N. J.

ELECTED NOVEMBER 10.

Billard, Jos. D., Jr., 71 Wall St., New York, N. Y.
Sturm, A. B., 2421 Dearborn St., Chicago, Ill.
Weber, C. E., 2421 Dearborn St., Chicago, Ill.

ELECTED NOVEMBER 20.

DuPont, Alexis I., Wilmington, Del.

CHANGES OF ADDRESS.

Barton, G. E., Hatfield, Mass.
Cary, J. S., 1760 Monadnock Block, Chicago, Ill.
Coombs, Frank E., Central Teresa, Ceiba Hueca, Manzanillo, Cuba.
Ewell, E. E., 1404 Stoughton St., Washington, D. C.
Latham, Woodville, 32 East 21st St., New York, N. Y.
Lehmann, A., 57 Bayersche St., Port 1, Leipzig, Germany.
Mar, F. W., 32 McDonough St., Brooklyn, N. Y.
Sargent, Geo. W., Boy's High School, Reading, Pa.
Smith, E. E., 157 East 74th St., New York, N. Y.
Spencer, Dr. G. L., 134 Rich Avenue, Mt. Vernon, N. Y.
Willet, Prof. J. E., Augusta, Ga.
Williams, W. J., 1412 Van Buren St., Wilmington, Del.

ADDRESSES WANTED.

Hahn, A. G. C., old address, 4 and 6 New Chambers St., New York, N. Y.
Ray, Victor, old address, Anaconda Electrolytic Refinery, Anaconda, Montana.